ANALYSIS OF A CHEMICALLY-BONDED PHOSPHATE CERAMIC AS AN ALTERNATIVE OILFIELD CEMENTING SYSTEM FOR ARCTIC REGIONS

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A

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Abstract

Traditional Portland cement has been used in the oilfield industry for over a hundred years in the United States. However, under the harsh cold of arctic conditions, cement has failed to provide the minimum standards of strength and safety required in the petroleum industry. Though there has been significant research to correct this shortcoming, no ideal solution has been found to improve the arctic performance of Portland cement.

A chemically-bonded phosphate ceramic, known generically as Ceramicrete, has been developed which appears attractive as a cement replacement in arctic well construction. This material contains no Portland cement and does not have its limitations under cold conditions. It uses the same equipment in terms of storage and production as the Portland cement. In this research, Ceramicrete was vigorously tested according to industry-specifications in order to compare its material behavior against that of Portland cement as a viable alternative under arctic oilfield conditions.

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Chapter 1:

1.0. Introduction

One of the most fundamental building blocks in the oil and gas industry is Portland cement. With over a hundred years of use in the field, significant work has been done to make cement a material adaptive to the specifications of widely different locations, each with its own unique geophysical needs and environmental conditions. A multibillion dollar industry now exists to cater to the need for cement extenders, densifiers, dispersants, heat treatments, and dozens of other products used to modify Portland cement for the varying needs of oilfield use. Despite massive investment into making cement workable for nearly any environment, no technology currently exists that makes cement an appealing material for arctic regions. Even as the oilfield industry continues in its use of Portland cement in freezing climates, the measured behavior of cement under the conditions of this environment can only be described as exceptionally poor, if not bordering on abject failure. In regions with operating temperatures below the freezing point of water, cement has demonstrated undesirable material properties such as shortened product life, poor strength-development, and high porosity (Goodman, 1977). As production increasingly shifts to areas like the Alaska North Slope, Siberia, northern Canada, and offshore locations, it becomes a growing necessity to both understand the unique cementing issues of cold regions and develop materials more suited for use in these cold climates. While the focus of this research is on the casing concerns of areas on

the Alaska North Slope, many of the conclusions and concerns may be equally applicable to other cold region oil and gas well cementing applications.

1.1. Definition of the Problem and General Temperature Limitations

Set Portland cement is a remarkably durable and adaptable material; however, there are limits beyond which the material will become less than desirable. In regions with temperatures below the freezing point of water, temperature effects become a dominant force in the development of cement's material properties. The primary issue in these cold regions is premature freezing of the cement slurry. Rather than seeing the slurry set and develop strength as expected, the slurry water within the poured product freezes to form a network of interconnected ice crystals within the setting product (Morris, 1970).

The presence of these ice crystals greatly affects the properties of the set cement. Ice has significantly different loading behavior than Portland cement, leading to a frozen product that is significantly weaker than a true set product. As a result, the ultimate strength of cement in cold regions tends to be nominal and is frequently below what is demanded from an engineering and safety perspective. Freezeback is another identified problem as well, when drilling or cementing operations pass through regions of thick permafrost. A conventionally cemented well is likely to thaw these permafrost regions, with the thaw zone extending as far as a meter or more beyond the boundary of the

wellbore (Nelson and Drecq, 2001). Casing collapse raises a serious concern in cold regions if no preventative steps are taken.

Furthermore, the existence of a connective network of ice crystals within the set product has the effect of increasing porosity. During the setting process, the formation of an ice network displaces the setting cement slurry, resulting in a mass of channels within the final product. While frozen, the ice network serves to fill and plug these channels, decreasing the effective porosity of the set cement product. However, the network is easily subjected to disruption by the heat of produced and/or drilling fluids, as well as by seasonal temperature changes. Upon sufficient heating, the ice network is disturbed and the effective permeability of the set product rapidly increases (Nelson and Drecq, 2001). Thus, a frozen cement wellbore casing is very likely to experience future problems with oil and gas migration, a costly and environmentally-damaging situation for a producing well.

Cycling temperature effects also decrease the product life of Portland cement when it is used in cold regions. Oilfield cements are not homogenous products but rather are composed of a collection of aggregates, namely a mixture of calcium, silicon and aluminum oxides ("Cement", 2004). Each aggregate has significantly varying coefficients of contraction and expansion. As the set product proceeds through several freeze-thaw cycles, the mismatch in these coefficients leads to internal stress within the product, surface and volume flaws, and the creation of microfractures within the cement.

As these microfractures grow and multiply, the fatigue-resistance of the cement is diminished by a large amount. As a result, arctic cementing jobs see the need for frequent repair and/or replacement (Wagh, 2004).

Finally, cement performs poorly as an insulation between the formation and wellbore. One primary function of a well casing in northern regions is that of an insulative barrier, protecting the surrounding formation from the heat of drilling, production, and possible fluid injection. In this regard, cement functions adequately, but improvements in these properties would be welcomed by the oil and gas industry. Should cement become more insulative, more work could be done in northern climates without fear of environmental damage, formation subsidence, or hole collapse (Smith, 1986). Table 1 summarizes the negative effects that sub-freezing temperatures can have on Portland cement and its performance as an oilfield borehole cement.

Table 1: Negative effects of cold temperatures upon Portland cement

General Temperature Limitations
• Premature freezing of the setting product
• Weakening of the final product
• Shortened product life
• Increased dangers of gas and oil migration

1.2. Ideal Cement Behavior

After careful consideration of the engineering problems inherent in arctic cementing, it becomes necessary to define the design elements which are significant for a permafrost cementing system. Cement for applications in a permafrost region should exhibit the following characteristics as enumerated by Morris:

1. The cement should be free of pores and voids to avoid freeze-thaw deterioration.
2. The cement should have little to no connective pore space to avoid oil and gas migration.
3. The thermal conductivity of the cement should be as low as possible.
4. The cement should exhibit sufficient load-bearing properties for applications as varied as that of wellbore casings and supports for pipelines.
5. The cement should exhibit good bonding with casing steel and earth materials such as formation rock. It should be self-bonding to allow for inexpensive repair jobs.
6. The cement slurry should provide 3 ½ - 5 hours of working time at downhole pressures and temperatures.
7. The cement should set at temperatures as low as 14° F (-10° C) without freezing or the need for external heat.
8. The cement should have as low a heat of hydration as possible.
9. The cement should have a wait-on-cement time of less than one day, developing a minimum of 500 psi of compressive strength within this time.

10. The slurry should not be reactive with those items it is likely to encounter downhole, including but not limited to drilling mud, Portland cement, hydrocarbons, and formation brines.

11. The set cement product should prove highly insulative so that injected fluids and drilling operations do not disrupt unconsolidated formations.

12. The slurry should provide a controlled rheology.

13. The slurry should have no free water.

14. The set product must provide stability to freeze-thaw cycling.

15. The cement should be bulk-blended and easily handled by field equipment and personnel.

1.3. Scope of the Research

One of the basic material requirements for oil and gas exploration in permafrost regions is a suitable insulating cement that will keep the permafrost region undisturbed during production and transportation of oil and gas. However, conventional Portland cements do not provide adequate insulation or material strength under these conditions. New approaches to cementing could help reduce the safety and environmental hazards created by cementing failures. Using the criteria outlined for an ideal cementing system, Ceramicrete is evaluated as a borehole cement for drilling through the permafrost/gas hydrate intervals in the North Slope of Alaska.

Chapter 2:

2.0. Literature Review

2.1. Limitations for Consolidated Formations

Until the discovery of large oil deposits in the Alaska North Slope, very little information had been collected on well completions in cold environments. In the 40 years since that time, the burgeoning oil industry in areas such as northern Canada, Russia, the Arctic Islands, and Alaska has led to significant research into proper oilfield practices for these environments. However, the techniques appropriate for a cold formation vary widely depending on the geological and physical properties of the cold formation (Maier, 1971).

In areas such as the Arctic Islands, the cold formation is fairly well consolidated. Consolidated formations are advantageous because thawing during drilling and cementing do little to disrupt the area surrounding the wellbore. As a result, there are few concerns about well practices that may lead to thaw subsidence, casing stress, hole collapse, or environmental damage. Freezing of a cement slurry can be prevented through external heating, such as the use of a warm displacement fluid. There is no particular need for specialty material use as the primary problem of freezing can be controlled through numerous measures, limited only by the environmental laws of the area. Table 2

summarizes various methods of slurry protection that are appropriate for a consolidated cold formation (Maier, 1971).

Table 2: Methods to avoid premature freezing in a consolidated frozen formation

Methods of Slurry Protection in Consolidated Formations
• Pre-heated slurry water
• Warm displacement fluid
• Localized heating of the air

Instead of modifying cement properties to meet the needs of the environment, one can temporarily change the environment to allow for proper setting of the cement. Heating of the slurry water, addition of a warm displacing fluid, or even localized heating of the air in areas of slurry placement can all raise the formation temperature above that of freezing, protecting the cement slurry from any adverse effects. A frozen consolidated formation that is unharmed by thawing can likely be cemented with any slurry that will adequately set at the existing curing temperature. However, in areas where the frozen formation contains ice lenses and is incompetent in the material sense, where the formation must not be allowed to thaw, specialized slurries must be called upon to do the job (Maier, 1971).

2.2. Limitations for Unconsolidated Formations

A more difficult problem arises during cementing operations in the unconsolidated permafrost/gas hydrate regions of the world, namely the Canadian Northwest Territories and the Alaska North Slope. In regions with unconsolidated formations, the use of an external heat source to prevent slurry freezing is not an effective or safe option (Maier, 1971). In these areas, drilling and cementing need to be accomplished with a minimum amount of thawing around the wellbore. Melting can cause the thawed formation to subside, particularly in the upper 200 ft of the well. If the permafrost melts, drag forces can be transferred from the soil to the casing. Furthermore, hole sloughing and possible collapse become realistic possibilities (Smith, 1986). For these reasons, no external heat source should be used to prevent freezing and the cement must itself exhibit a low heat of hydration.

Permafrost behavior varies greatly depending on region. The Mackenzie Delta and other continental regions of Canada, for example, exhibit shallow formations frequently consisting of ice lenses and frozen muskegs (Davis, 2001). By contrast, Alaska has permafrost with no real consistency, varying greatly depending on the area of the state in which drilling is occurring. Permafrost thins out in the ocean and lake areas, and disappears completely offshore in water depths of 10 ft or more. The permafrost also varies in ice content, with some sections showing as little as 20% ice and others as much as 90%. Permafrost in the arctic region of Alaska at times resembles snow, while

elsewhere ice lenses can vary in thickness from a fraction of an inch to several feet. The permafrost in these arctic regions is reported to vary from unconsolidated sands and gravels with ice lenses to some areas of ice-free, consolidated rock (Davis, 2001). For this reason, permafrost is defined only in the broadest of possible terms, generally described as a formation whose soil remains frozen for two consecutive years. The depth of this permafrost soil may vary from 500 feet to 2000 ft, depending on location, with the permafrost temperature varying from 15 °F to 32 °F (-9.4° to 0 °C) (Davis, 2001).

State of Alaska environmental conservation laws and regulations dictate that drilling and cementing operations in Alaska must have minimal environmental impact on regions of permafrost (a rule of thumb describes this as the upper 300 ft. of a formation) (Alaska Code, 2004). Thus, formation thaw protection becomes not only sensible industry practice but a legal requirement. More information on these laws can be found in Alaska statute 20 AAC 25.030, presented in Appendix A.

2.3. Current Industry Practices

Currently, there is no standard casing program for well completions in permafrost regions. Each area has a different casing design based on the drilling objectives of that particular well and upon the economics of the field. One standard practice is to set all surface pipe several hundred feet below any permafrost and cement it back up to the surface. Surface casings of 3,000 to 4,000 ft are not uncommon (Smith, 1986). Numerous

additional precautions must be taken in a permafrost area, including the use of high-strength ductile casing designed for sub-freezing conditions, casing designs that protect the formation from injection fluids and warm oil produced over the life of the well, and the need to leave no fluid in the annulus that might freeze and damage the casing.

Field experience has shown that the cement casing needs to show only a minimal amount of early strength for drilling operations to continue. Acceptable Wait-On-Cement (WOC) times are less than one day, but after this time the set product need only provide approximately 500 psi of compressive strength. An experienced field engineer may be capable of working with as little as 250 psi of strength in 24 hours time, though 500 psi is a more appropriate measure for safety reasons (Benge, 1982). Most slurries in the permafrost region, regardless of composition, must have a working time of 2 to 4 hours because the larger pipes used require more cement than normal, thus requiring more placement time. A safety margin for unexpected problems is also included in this working time (API Spec. 10, 2004).

2.4. Background Information on Portland Cement

Portland cement is the most common type of cement in general usage, as it is a basic ingredient of both concrete and mortar. As stated earlier, it is composed of a mixture of various oxides, most commonly calcium, silicon, and aluminum. Portland cement, and similar materials, is made by heating limestone with clay or sand and then

grinding the product. The resulting powder, when mixed with water, will become a hydrated solid over time (Banfill, 2003).

Production of Portland cement is broken into three fundamental stages:

1. Preparation of the raw material
2. Production of the clinker
3. Final preparation of the cement

The raw materials for Portland cement production are calcium oxide, silicon oxide, aluminum oxide, ferric oxide, and magnesium oxide, in the proportions illustrated in Figure 1.

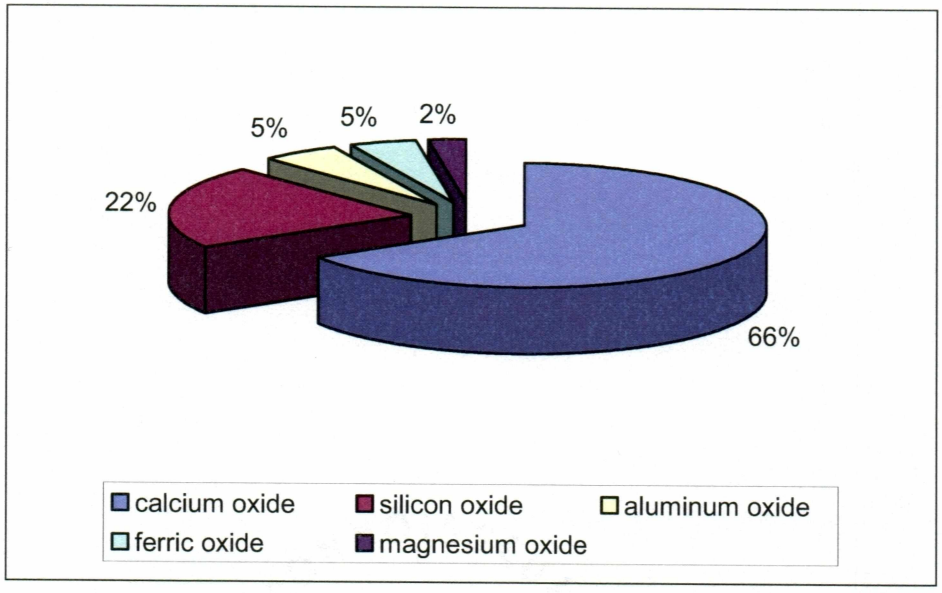


Figure 1: Raw materials required for Portland cement clinker

The production of clinker can be described as follows as follows (Wikipedia, 2004):

> "The raw mixture is heated in a kiln, a gigantic slowly rotating and sloping cylinder, with temperatures increasing over the length of the cylinder to roughly 1480° C. Temperature regulation is especially important during this sintering process, as too low a temperature causes insufficient sintering but too high a temperature results in a molten mass or glass-like product. In the lower temperature part of the kiln, calcium carbonate turns into calcium oxide and carbon dioxide. In the high temperature part, calcium oxides and silicates react to form dicalcium and tricalcium silicates. Small amounts of tricalcium aluminate and tetracalcium aluminoferrite are also formed."

The resulting material is clinker, which is pulverized into a powder with roughly 2% gypsum by weight. The finished cement has approximately the following composition: calcium oxide (64%), aluminum oxide (5.5%), silicon oxide (21%), ferric oxide (4.5%), magnesium oxide (2.4%), and sulfate (1.6%) (Wikipedia, 2004). This make-up is graphically illustrated in Figure 2.

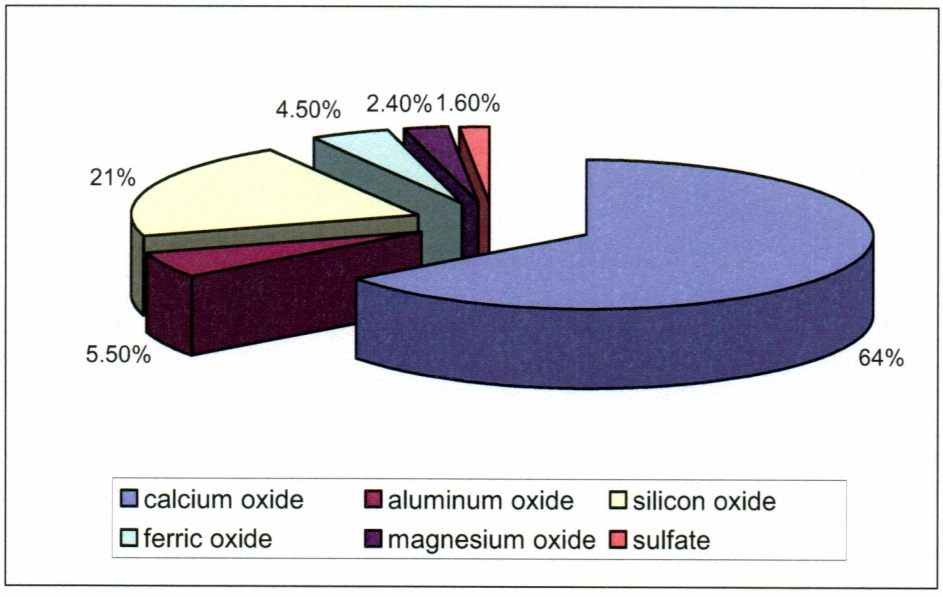


Figure 2: Composition of Portland cement

2.5. The Use of Freeze-Depressing Additives

Early work in freeze-protected cementing systems made extensive use of freezing point depressants for the slurry water. Many different materials were used, including salts, alcohols, and specialty polymers, with varying success. However, one trend remained consistent across all the additives that were used: in quantities necessary to prevent the freezing of the slurry water, additives had a side-effect of making the set cement product weak to the point of uselessness. Thus, the use of additives has been abandoned as a primary solution to the freezing problem, and additives are used only in conjunction with other freeze-prevention methods, such as specialty extended permafrost systems (Nelson and Drecq, 2001).

2.6. Existing Extended Permafrost Systems

2.6.1. High-aluminate Cements

Calcium aluminate cements are special-use cements of limited production and premium price. Their general use is for preparing fire-brick mortar; however, they are gaining wider acceptance for industrial use and for cold-weather construction. The high-aluminate cements contain no free lime and none is produced upon hydration, as is the case with the American Petroleum Institute (API) classes of cement; therefore, adding fly ash or pozzolans creates only diluents and no cementitious reaction occurs (Smith, 1986).

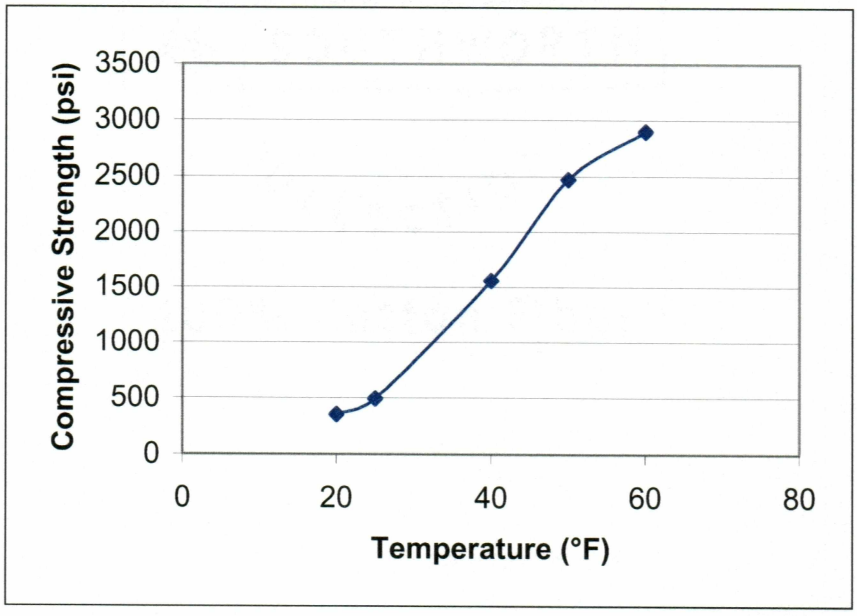


Figure 3: Strength development of calcium aluminate cements at different temperatures (Nelson and Drecq, 2001)

As shown in Figure 3, high aluminate cements will set and gain strength rapidly at low temperatures, reaching about 95 percent of the ultimate strength in 24 hours. These cements exhibit a high heat of hydration, and since the hydration reaction occurs rapidly, high cement-column temperatures may occur. Performance characteristics of these cements change drastically with the addition of small quantities of other materials. Sodium chloride will severely retard the setting time; lime, calcium chloride, and the API classes of cements may cause an instantaneous (flash) set. Extreme care must be taken to avoid contamination (Smith, 1986). Besides contamination, another concern with calcium aluminate cements is degredation. Degradation occurs if the cement becomes warm and moist. Degredation is caused by a change from a metastable crystalline structure to a cubic form and is accompanied by a color change from near black to a reddish brown (Smith, 1986).

Through the use of chemical extenders and freeze depressants, a high-alumina cement can be used to make a highly extended permafrost cement system. The system exhibits a heat of hydration great enough to enhance the setting process, but uses large quantities of water to moderate the heat generated during hydration, eliminating the need for fly ash (Benge, 1982).

Unlike Portland cement, whose principal constituent is tricalcium silicate, the principal constituent in high alumina cements is mono-calcium aluminate. During hydration of Portland cement, mono-calcium silicate is formed and lime is liberated. For

high alumina cements, hydration forms dicalcium aluminate, with alumina liberated in place of lime. The chemical reaction in high alumina cement generates heat much more rapidly than the reaction in Portland cement (Nelson and Drecq, 2001).

A high-alumina cement cannot be blended with Portland cement, since blending of the two will cause extreme acceleration of the high-alumina cement, resulting in severe gelation or "flash" setting. Operators must use extreme caution to prevent contamination of a high alumina cement system with Portland cement. The chance of contamination can be minimized with astringent cleaning of field bins, bulk trucks and storage facilities before and after each job using a high alumina cement system. However, under normal operations it becomes almost impossible to eliminate the chance of cross-contamination.

High alumina cements have been used to cement through the permafrost both in Canada and on the Alaska North Slope. Two high-alumina cements have been marketed under the tradenames of Luminite and Ciment Fondu (Nelson and Drecq, 2001).

2.6.2. Gypsum-Cement Blends

Gypsum-cement blends, with a mixing-water freezing temperature depressant, have unique properties that make them attractive for low and freezing subsurface temperature environments. The gypsum phase sets and gains strength rapidly at these temperatures, providing adequate strength for continuing well operations. Protected from

freezing, the more slowly setting Portland cement phase then hydrates, providing the cement with high ultimate strength and durability (Maier, 1971).

Figure 4 illustrates how gypsum-cement slurries were designed for use at temperatures between 80° F and 15° F (26.7° to -9.4°C), with salt added to help prevent freezing at temperatures less than 32° F (0° C). Like conventional cements, gypsum-cement slurries also become exceptionally permeable if allowed to freeze before setting. A very low heat of hydration is realized, less than 20 BTU per lb of slurry (Maier, 1971).

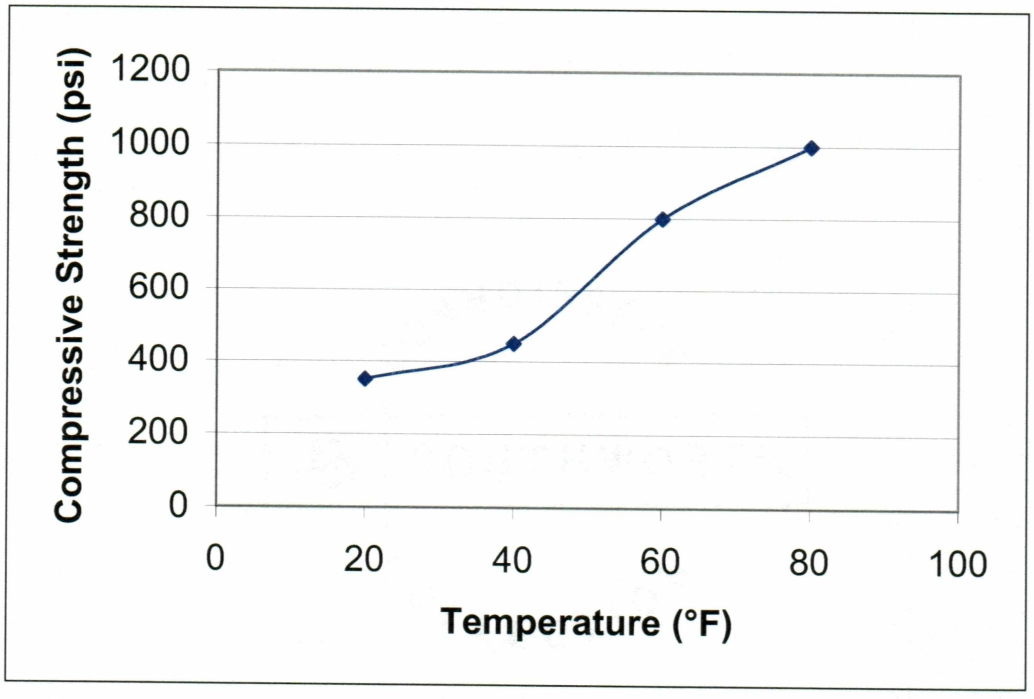


Figure 4: Strength development of gypsum cements at varying temperatures (Nelson and Drecq, 2001)

Though these gypsum-cement blends have become the primary method of cementing in permafrost areas, they have significant drawbacks. Additional freezing point depressants need to be added to the slurry water, and strength development is poor when compared to conventional Portland cement or even calcium aluminate cements. Furthermore, a high cost makes gypsum-cement blends less than ideal for widespread use.

Chapter 3:

3.0. The Development of Chemically-Bonded Phosphate Ceramics (Ceramicrete)

Chemically-bonded phosphate ceramics are formed by an acid-base reaction between an acid phosphate (e.g., potassium, ammonium, or aluminum) and a metal oxide (e.g., magnesium, calcium, or zinc) (Wagh, 2001). A powder blend of the two is mixed with water to make a slurry. The slurry sets at room temperature within minutes or hours, depending on the additives. It forms a dense ceramic that can be tailored to develop desirable properties. Though this material maintains a number of desirable ceramic properties, such as high strength and thermal resistivity, it sheds the energy intensive process of sintering that most non-silicon based ceramics require to obtain their final shape and material properties (Wagh, 2004).

Ceramicrete is a trade name given to the process of generating magnesium potassium phosphate ($MgKPO_4 \cdot 6H_20$) by reacting magnesium oxide (MgO) with a solution of potassium phosphate (KH_2PO_4). Developed at Argonne National Laboratory (ANL), this novel form of ceramic production was originally intended for the stabilization and transport of radioactive and hazardous waste (Wagh, 2003). Since its

development, the material has undergone some adaptation for niche applications where the properties of a ceramic may be desirable but the workability of cement is needed. In the case of oilfield operations, research has been performed by ANL to increase the strength and insulative properties of Ceramicrete while also reducing the cost of the material to allow it to compete with the price-point of existing oilfield solutions. The permafrost-formulation of Ceramicrete has seen the addition of c-class fly ash and wollostonite to improve material properties. Fly ash is a common industrial byproduct, both cheap and easily acquired in bulk quantities. In addition to increasing the strength of the final set product, fly ash adds to the insulative properties of Ceramicrete and will reduce the cost of the blended powder. Additionally, by adding fly ash one mitigates the exothermic reaction of Ceramicrete, reducing its thawing effect upon the surrounding formation. Wollostonite, like fly ash, adds to the strength and thermal resistivity of Ceramicrete, but also adds a thickening effect to the Ceramicrete slurry (Wagh, 2004).

A major advantage that Ceramicrete possess over other possible cement alternatives is that, despite a novel chemistry, handling techniques for Ceramicrete are no different than those for conventional cement. No new equipment or training is required for the use of Ceramicrete, and the hardened product can be assumed to behave in an equivalent manner to cement. A Ceramicrete slurry, in the field, would be prepared by bulk mixing a dry mix powder with water in a batch mixer, just as with Portland cement. The set product has an appearance and texture similar to that of cement, and like cement exhibits the ability to bond to itself, to formation materials, and to steel (Wagh, 2001).

3.1. Dissolution Model for Ceramicrete Production

3.1.1. Dissolution of Oxides and Formation of Sols by Hydrolysis

Generation of a Ceramicrete product begins with the dissolution of potassium phosphate (KH_2PO_4). As dissolution of this chemical occurs, two key effects are obtained: first, the addition of free phosphate serves as a freezing point depressant for the water in solution, while a secondary effect is the evolution of a high acidity environment. When metal oxides are stirred into an acid solution, the oxide generally separates into two component parts, a metal cation as well as an oxygen-containing anion. The metal cation reacts with free water molecules and forms positively charged 'aquasols' by hydrolysis. In the case of MgO, the generation of these aquasols is dependent on a solution pH lower than 12. Any mildly acidic solution is more than suitable for the creation of chemically-bonded phosphate ceramics (Wagh, 2003). The key reactions formulas are present below.

$$KH_2PO_4 \leftrightarrow 2H^+ + KPO_4^{2-} \text{ (Dissolution of phosphate)} \quad 3.1$$

$$MgO + 2H^+ \leftrightarrow Mg^{2+} + H_2O \text{ (Dissolution of metal oxide)} \quad 3.2$$

$$Mg^{2+} + H_2O \rightarrow [Mg{*}H_2O]^{2+} \text{ (Formation of aquasol)} \quad 3.3$$

The dissolution and hydrolysis of these metal cations are the controlling step in the formation of chemically-bonded phosphate ceramics. To drive this reaction forward, use of Le Chatalier's principle is judiciously used in the creation of the Ceramicrete blend. An excess of KH_2PO_4 drives the reaction forward towards the creation of a ceramic product, and pushes the hydrolysis of Mg^{2+} cations to restore equilibrium. The dissolution rate of KH_2PO_4 is far less of a concern, chemically, as this chemical has a remarkably high rate of dissolution (Wagh, 2003).

3.1.2. An Acid-Base Reaction and Formation of a Gel by Condensation

The aquasols generated by the hydrolysis of Mg^{2+} react with the aqueous phosphate anions to form hydrophosphate salts. Reacting in parallel, free protons and oxygen react to form water. The newly formed hydrophosphate salts react together to form a network in the aqueous solution that leads to the formation of a gel composed of magnesium potassium phosphate, as shown below (Wagh, 2003).

$$H^+ + Mg(OH)^+ + KPO_4^{2-} + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O \qquad 3.4$$

3.1.3. Saturation and Crystallization of the Gel into a Ceramic

As the reaction proceeds, more and more hydrophosphate salts are "added" to the gel and the Ceramicrete slurry thickens. This creation of a gel structure is identical to the

sol-gel process of non-silicate ceramics. As increasing numbers of cations are released into the colloidal gel solution, previously isolated sols experience a condensation reaction and become connected to other sols. Chains of connected sols begin to form and percolate throughout the solution to form a gel (Wagh, 2003).

When sufficiently thickened, the gel is essentially a saturated phosphate solution in which a significant amount of undissolved metal oxide particles remain and are uniformly distributed. As precipitation of the phosphates occurs, these metal oxides provide nucleation points for crystallization into a well-connected crystal lattice. Thus it is important that some unreacted particles are available to provide a good stable ceramic. Formation of a well-crystallized ceramic or a poorly crystallized precipitate will depend on how rapidly the dissolution of the oxides occurs in the acid solution. The overall acid-base reaction is exothermic and heats the reaction slurry; if the reaction temperature is higher than the boiling point of the slurry, the slurry will boil over and disrupt the formation of the ceramic. Thus, upper and lower boundaries of ceramic production are adopted according to the dissolution of the metal oxide: high oxide solubility results in a precipitate, while low oxide solubility will result in a non-reaction (Wagh, 2003).

3.2. Effects of Boric Acid on Solubility of MgO

In large batches, Ceramicrete has a mixing time of only a few minutes before the exothermic acid-base reaction begins between MgO and KH_2PO_4. Therefore, chemical

retardants are necessary for any sort of large-scale mixing operation. Boric acid is useful for this purpose. When a very small quantity of boric acid is mixed into a Ceramicrete powder blend, a coating develops on the MgO particles and retards early dissolution, thus delaying the acid-base reaction (Wagh, 2003). The reaction leading to the coating of MgO is shown in the formula below:

$$3\ MgO + 2\ H_3BO_3 + 2\ H_3PO_4 \leftrightarrow Mg_3B_2(PO_4)_2(OH)_6{\cdot}H_2O + 2H_2O \qquad 3.5$$

The addition of boric acid to the powder blend leads to the creation of a polymeric coating upon MgO, identified by X-ray diffraction in the literature as lunebergite. When boric acid containing MgO is mixed into the phosphate solution, lunebergite is formed on the grains of MgO and coats them. This prevents the grains from dissolving into the acid solution. Subsequently, as the pH of the solution rises, the coating slowly dissolves and exposes the grains back to the acid solution. Thus, because the dissolution of MgO is delayed, the rate of dissolution is reduced and the acid-base reaction is retarded (Wagh, 2003).

Chapter 4:

4.0. Experimental Procedure and Testing Methodology

In preparing a cement slurry, a number of laboratory tests can be conducted to predict and evaluate the performance of the slurry as it is pumped and after its placement. The majority of these tests are standardized by the American Petroleum Institute (API), and this organization has outlined critical cement properties for the oil and gas industry and appropriate methods to assess these properties. Though a number of competing standards exist, as produced by the Construction Specification Institute (CSI) and the American Standards for Testing of Materials (ASTM), the API standards were used, when available, for this research work to evaluate the material properties of Ceramicrete and compare it to the equivalent behavior of Portland cement.

Table 3 provides a summary of tests traditionally used in cement slurry-design, as well as the API test reference document. Though not all of these tests were performed as part of the scope of this thesis, the majority of these evaluative criteria were used for Ceramicrete. Additional tests were performed to further define the novel material characteristics of this phosphate-based ceramic.

Table 3: Summary of tests used in cement slurry design

Slurry Property	Laboratory Test	Test Reference
Slurry preparation for laboratory mixing and testing	Balances and high-shear mixers	API Document 10, Sec. 5
Slurry viscosity	Atmospheric thickening-time tester	API Document 10, Sec. 9
Pumping time	Consistometer testing	API Document 10, Sec. 8
Free water	Settling of slurry in 250-ml graduate after setting	API Document 10, sec. 5
Fluid loss of cement slurry	High-pressure fluid-loss cell at 1,000 psi on 325 mesh screen for 30 minutes	API Document 10, Appendix F
Slurry density	Standard Mud Balance	API Document 10, Appendix C
Rheological properties	Rotational viscometer at various shear rates	API Document 10, Appendix H
Permeability testing	Special water permeability apparatus for set cement	API Document 10, Appendix G

4.1. Ceramicrete Formulation

The Ceramicrete formulation used in the experimental testing of this study was a combination of MgO (25 % by weight), KH_2PO_4 (27.2 % by weight), c-class fly ash (10.2 % by weight), wollastonite (10.2% by weight), boric acid (0.09 % by weight), and water (27.2 % by weight). Unless stated otherwise in the text, it should be assumed that any reference to Ceramicrete is composed of this formulation.

A summary of tests performed upon this formulation of Ceramicrete is as follows:

1. Thickening time testing
2. Freeze-resistant setting tests
3. Thermal conductivity tests
4. Heat of hydration test
5. Reactivity to hydrocarbons
6. Reactivity to Portland cement
7. Determination of slurry pH
8. Slurry density measurements
9. Connective porosity measurements
10. Cement rheology measurements
11. Uniaxial compressive strength tests
12. Splitting tensile strength tests

13. SEM analysis

4.2. Thickening Time Testing

Thickening time testing, also referred to as consistometer testing, measures the length of time a slurry will remain in a fluid state under simulated downhole conditions without any shutdown periods. The testing apparatus, known as a consistometer, consists of a rotating cylindrical slurry container that envelops a stationary paddle. This slurry container is in turn encased within a pressure vessel and surrounded in a "heating" fluid that can manipulate the operating temperature. In the course of this research, a Chandler Engineering Model 5270 (Figure 5) consistometer was used, running DAC 1.0 software and using mineral oil as the heating fluid.

Figure 5: A photo of a Chandler-brand consistometer

A conventional consistometer, however, is unable to simulate sub-freezing temperature conditions. Thus, modification of the apparatus was necessary. This apparatus was modified by attaching a Thermo Neslab m75 source cooler (Figure 6) to the device; the mineral oil used as heat exchanging fluid was run through the cooler to provide the sub-freezing temperatures that would be experienced downhole. A downhole pressure of 1500 psi was simulated in all test cases with an operating temperature of 32°F (0°C).

Figure 6: A Thermo Neslab m75 cooler

As the consistometer maintains the slurry at the desired pressure and temperature, the torque on the stationary paddle is measured and converted by the DAC 1.0 software into a slurry consistency, measured in Bearden units (Bc). The limit of pumpability is reached when the slurry reaches a consistency of 70 Bearden units, as established in API standard 10.

The API specifies that an oilfield cement should exhibit a pumping time ranging from 3 ½ to 5 hours. This recommendation depends largely on the intended purpose of the cement slurry and the volume that is being pumped. For shallow depth cement placements or high-temperature deep liner jobs, a pumping time of 3 to 3 ½ hours is sufficient as these cementing jobs rarely require more than 90 minutes for slurry placement. In contrast, spotting a cement plug requires thickening times of less than 2 hours while squeeze cementing jobs require greatly varying times (API Spec.10, 2004).

Upon completion of consistometer-testing, the Ceramicrete slurry is sufficiently mixed and thickened to prepare a set product. In the remainder of this work, if a slurry is referenced for further testing, it should be assumed that the slurry is the thickened and mixed slurry prepared through a consistometer-run unless stated otherwise.

4.3. Freeze-resistant Setting

Freeze-resistant setting was measured by filling plastic cylindrical molds with the Ceramicrete slurry prepared during the consistometer-testing. These molds, measuring 2-in. by 4-in., were then placed in refrigerated areas and allowed to set for 24 hours at varying temperatures. The selected setting temperatures were 68° F (20° C), 59° F (15° C), 50° F (10° C), 41° F (5° C), 32° F (0° C), 23° F (-5° C), and 14° F (-10° C). After 24 hours, samples were removed from refrigeration and examined for signs of freezing.

Signs of freezing included the visible presence of entrapped ice or hoar frost, the appearance of enlarged pores, or thaw-softening of the set product within two hours of removal from refrigeration.

If no thaw softening occurred, the prepared sample was returned to its original refrigeration temperature for further testing. If a set sample is referred to in this text, it should be assumed that these samples cured at low temperatures are used unless otherwise stated.

4.4. Thermal Conductivity Tests

Thermal conductivity tests were performed by researchers at ANL on a disc-shaped sample of Ceramicrete roughly 4-in. in radius. The disk was insulated on the flat, broad circular surfaces using Styrofoam, leaving only the circumference of the sample disk exposed. Two J-type thermocouples were placed on the outer surface of the sample, resting on the center and circumference of the sample disc. The prepared sample was then placed in a 39.2° F (4° C) refrigeration unit overnight so that the sample would reach a uniform temperature of 39.2° F (4° C). Upon removal of the sample disk from the refrigeration unit, thermocouple readings were continuously recorded until the disk had equibrilated to room temperature 68° F (20° C).

It was assumed that by insulating the broad surfaces of the sample disk, thermal flow occurred only along the circumference of the sample. By further assuming that there was negligible variation along the thickness of the disk, heat flow is reduced to a one-dimensional model. Using this assumption and the time required for the center of the disk to reach room temperature, the thermal conductivity of the material was calculated (Cengel, 2001).

4.5. Heat of Hydration

Heat of hydration is traditionally measured using a calorimeter, an insulated vacuum flask containing a thermocouple connected to a recorder. The setting of both Portland cement and Ceramicrete is exothermic, with the heat of evolution increasing relative to the mass of the material that is setting. In place of this empirical method of measurement, researchers at ANL used an analytical method to establish the heat of hydration. Reference values for the heat of formation were established, with a difference calculation used to determine the heat of reaction for Ceramicrete.

4.6. Reactivity to Hydrocarbons

Reactivity to hydrocarbons was determined by ANL researchers by conducting consistometer tests in which the Ceramicrete slurry contained small pieces of dry ice.

During the testing procedure, this dry ice would react with the free slurry water and release carbon dioxide into the slurry as it thickened. By qualitatively judging the setting behavior and set product produced by these slurries, conclusions as to the reactivity of Ceramicrete to hydrocarbons can be drawn (Wagh, 2004).

4.7. Reactivity to Portland Cement

Reactivity to Portland Cement was tested by adding Portland cement impurities to a Ceramicrete slurry before consistometer testing. Both unreacted Portland cement powder and pulverized set Portland cement were added individually to a Ceramicrete blend producing compositions of 10%, 25%, 30%, and 50% of the total blend by weight. The set Ceramicrete product, inclusive of these impurities, was then tested using a uniaxial compression test to determine the affect of Portland cement impurities on the ultimate compressive strength and general mechanical properties of the Ceramicrete product. The test variables of the uniaxial compressive test are outlined later in this methodology section.

4.8. Slurry pH

Slurry pH was measured upon conclusion of a thickening time test. A Hanna Digital pH meter (Figure 7) was immersed in the slurry and the pH was directly read and recorded from the digital measurement.

Figure 7: Photo of a digital pH meter

4.9. Slurry Density Measurements

Slurry density was measured by filling a bulbed flask of known volume with Ceramicrete slurry, post-consistometer testing. By measuring the change in mass for the flask, the slurry density is easily calculated by dividing the change in mass by the volume of the flask.

4.10. Connective Porosity Measurements

Connective porosity measurements were taken at both ANL and UAF using cylinders of the set Ceramicrete product. An initial mass reading for these cylinders was taken, after which the sample was submerged in a tub of water for a period of 24 hours. After the 24 hour period, the sample was removed, shaken gently to remove droplets clinging to the sample, and was remeasured to detect any change in mass. Assuming a constant density for fresh water and that all open pores were filled during the submergence period, the volume of the connected porous space was calculated for the material.

4.11. Cement Rheology Measurements

Cement rheology measurements were done using a test that measures the deformation and flow of matter and emphasizes the relationship between stress, strain, rate of strain, and time. Cement slurries exhibit non-Newtonian behavior and their flow is traditionally described by one of two mathematical models, namely the Bingham plastic model or the power-law model (Banfill, 2003). To measure the rheological properties of the Ceramicrete slurry, an Ofite Model 900 automated viscometer (Figure 8) was used. This machine is a direct-indicating, rotational viscometer consisting of two integral parts: an outer sleeve and an inner bob. During testing, the outer sleeve is rotated at a constant revolution per minute setting. This sleeve rotation causes a torque on the inner bob that is

measured by means of a torsional spring dial. The Ofite Model 900 is preprogrammed to perform API rheology tests, and as such will take readings of rotational speed at 30, 60, 90, 100, 200, 300, and 600 RPM. Two sets of readings at each rotational speed were recorded, one as the rotational speed was ramped up and one as the rotational speed was ramped down. In addition, static gel strengths were measured at the end of the test as the slurry was left in a static state for 30 seconds and then again for a period of 10 minutes.

Figure 8: An Ofite Model 900 viscometer

4.12. Uniaxial Compressive Strength Test

The uniaxial compressive strength test (UCS), is an established test to determine both the strength of the cement and Wait-On-Cement (WOC) time. This test involves compressing a cylindrical sample under a flat metal plate at a constant rate. The load on

the sample is increased at this rate until the sample fractures under the applied force. Fracture is identified by a sudden decrease in resistance to loading, as well as a loud noise from the brittle sample. Sample cylinders are generally 4-in. in length and 2-in. in diameter though this varies slightly. The planes of the sample that are parallel to the loading plate must be polished to ensure uniform loading, leading to a reduced height to the sample cylinder (Hudson, 1997). A pneumatic compression testing device was used to provide the load at a rate of 0.2 lbs/second. The enclosed piston is shown in Figure 9, while the data collection apparatus is shown in Figure 10.

Figure 9: Compression testing piston

Figure 10: Compression testing data measurement setup

The choice of the length of the specimen represents a design compromise. In cases where samples have a large length-to-diameter ratio, *L/d,* the sample is likely to experience buckling during a UCS test. If this happens, the test results are meaningless as a measure of the fundamental compressive behavior of the material. Instead, the data will reflect more on the presence of unavoidable small imperfections of geometry and upon sample alignment with respect to the testing machine, both of which will become dominant driving forces behind specimen buckling. For this reason, the *L/d* ratio must be restrained to collect informative compressive data (Dowling, 1999).

Conversely, if *L/d* is excessively small, the test result is affected by the end-effects. As the specimen is compressed, the diameter of the cylinder increases due to the Poisson effect. Friction between the sample and the compression plate retards this motion at the ends, resulting in deformation of the sample into a barrel shape. This deformation is not truly characteristic of the material, and invalidates collected data on the material under compression. Although this effect can be minimized through certain methods (e.g., lubricating the ends), it is difficult to avoid entirely. As a result, in materials capable of large degrees of deformation in compression, the choice of a too small a *L/d* ratio may result in a situation where the behavior of the specimen is dominated by the end effects (Dowling, 1999). From previous discussion, the test will not measure the fundamental compressive behavior of the sample should this end effect occur.

Considering the desirability of both a larger *L/d* to avoid buckling and a small enough *L/d* to avoid end effects, a reasonable compromise is *L/d*=3 for ductile materials. However, for more brittle materials like Ceramicrete, the literature recommended value of *L/d* is instead on the order of 1.5 or 2 (Dowling, 1999). With these *L/d* values, the small amount of deformation that occurs causes little difficulty with end effects. Many materials that are brittle in tension will not be as brittle in compression. Tension-specific brittle materials that exhibit this behavior do so because they contain cracks or pores that grow and combine to cause failures along the planes of maximum tension. In concrete, this is particularly apparent at the boundary between aggregates. In compression, however, such flaws have much less effect, resulting is a compressive strength significantly higher than tensile strength for brittle materials.

Where compressive failure does occur, it is generally associated with a shear stress, so that the fracture is inclined relative to the specimen axis. This type of fracture is evidenced in Figure 11.

Figure 11: Ceramicrete compression samples pre- and post-fracturing

4.13. Splitting Tensile Strength Test

The splitting tensile strength test (STS) is a simple test that makes use of a pneumatic press to apply a diametral compressive force upon a sample cylinder. Commonly referred to as a "Brazilian Test", this is perhaps the most popular of a number of indirect tensile tests. Currently, the API has no approved testing procedure to examine the tensile strength of oilfield cements. As a result, the methodology outlined in ASTM standards and literature is used in this investigation. In this procedure, a sample cylinder is placed between the plates of a compression-testing machine, buffered only by two thin layers of plywood that serve as bearing strips (Heinhold, 2003). A diametral compressive force is applied upon the sample cylinder, generating an almost uniform maximum tensile

stress along its diameter. The primary mode of failure occurs with the splitting of the cylinder in or close to the diametral plane, as in Figure 12.

ASTM standards allow for the tested concrete cylinder to be of varying aspect ratios, though samples measuring 2-in. by 4-in. were consistently used throughout these tests. A hydraulic compression device was used to provide the compression-loading, with the exerted force increasing at a steady rate of 0.2 lbs/s until mechanical failure of the specimen occurred.

A number of limitations exist in the STS test because this is an indirect method of testing. A key limitation is that the stress generated in this test cannot be considered uniaxial, due to the presence of significant compressive normal stress in a horizontal direction. Additionally, there exist concerns that the failure mode in the STS test is artificially dominated by shear fracture initiation near the plate contact points (Heinhold, 2003). To reduce these concerns, the plywood bearing strips have been introduced into the ASTM testing method, as recommended by literature, to have fracturing occurring in a mode similar to that shown in Figure 12. These strips are roughly 1-in. wide, 4-in. long, and have a nominal thickness of 1/8 in. By distributing the force of compression over an arc along a portion of the cylinder circumference, the likelihood of failure due to a shear fracture decreases while stresses within the sample remain unaffected.

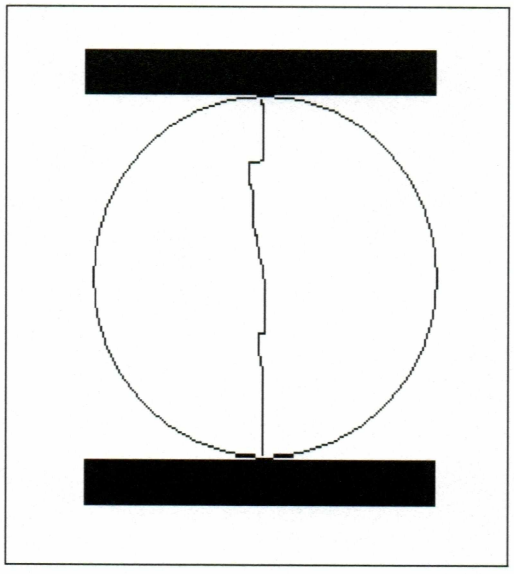


Figure 12: Illustration of how samples fail during STS

4.14. Scanning Electron Microscopy Analysis

Scanning electron microscopy was used to qualitatively analyze the set Ceramicrete product. Microscopy has a well-established history in the analysis of cement blends and is commonly used in the identification of blend quality and to detect differences among the various API cement classes. These differences reflect fundamental parameters that are unique to each cement and supplement the standard chemical and physical analysis techniques. These parameters have also been related to the slurry response properties in a qualitative manner.

In the analysis of Ceramicrete, SEM photography provides a graphical comparison between the macromolecular structures of the ceramic and conventional Portland cements. It also provides a means to visually inspect the set product for high porosity, deviations in the lattice structure, and microfractures that will likely reflect a shorter product life. Though qualitative in nature, SEM techniques allow for a wealth of information to be gathered to support the chemical and physical tests outlined in this methodology.

Chapter 5:

5.0. Results and Discussion

5.1. Thickening Time Testing

Multiple consistometer tests were performed using the defined Ceramicrete powder blend, with each test occurring at a pressure of 1500 psi and a temperature of 32°F.

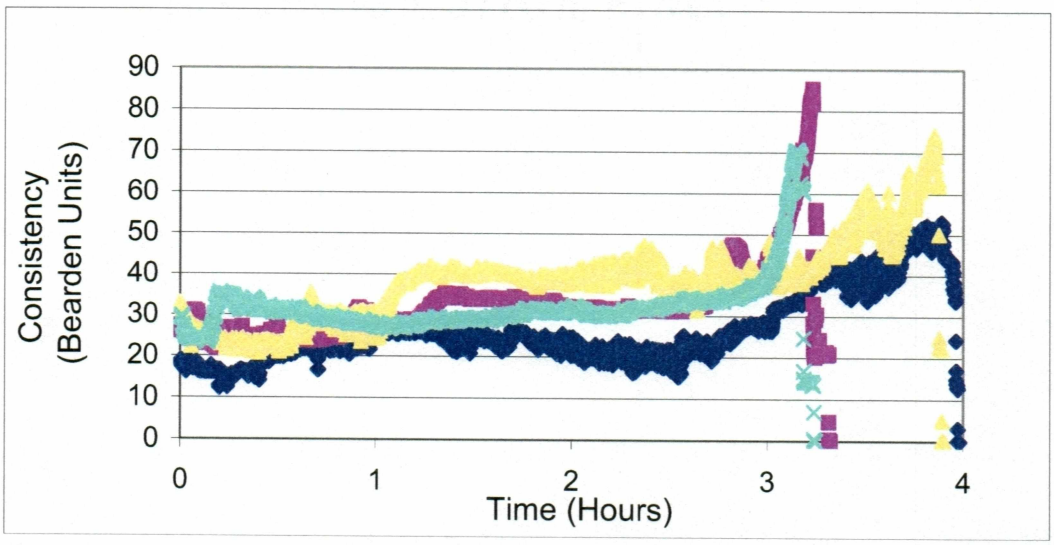


Figure 13: Multiple consistometer runs show Ceramicrete has a pumping time in the range of 3.5 to 4 hours

Though Figure 13 shows that all runs provided a pumping time within the API specifications of 3 ½ to 5 hours, there was a notable lack of internal consistency, with a group of pumping time run measurements clustering at nearly four hours and another group at 3.5 hours.

Individual run measurements deemed representative are illustrated in Figures 14 through 18. It can be seen from these figures that the pressure and temperature conditions of the slurry change with time. Also, the consistency changes as a result of extended churning under these conditions. It is important to note that the rate of change of pressure, temperature, and consistency is not reproduced exactly from consistometer test to consistometer test.

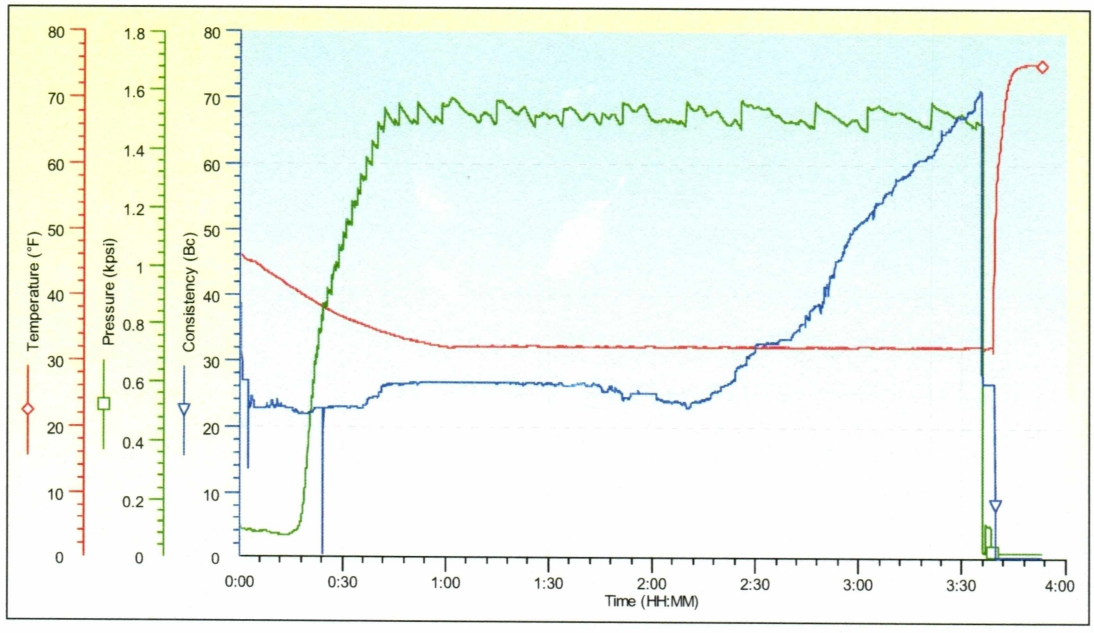


Figure 14: Consistometer run #1, 1500 psi and 32°F

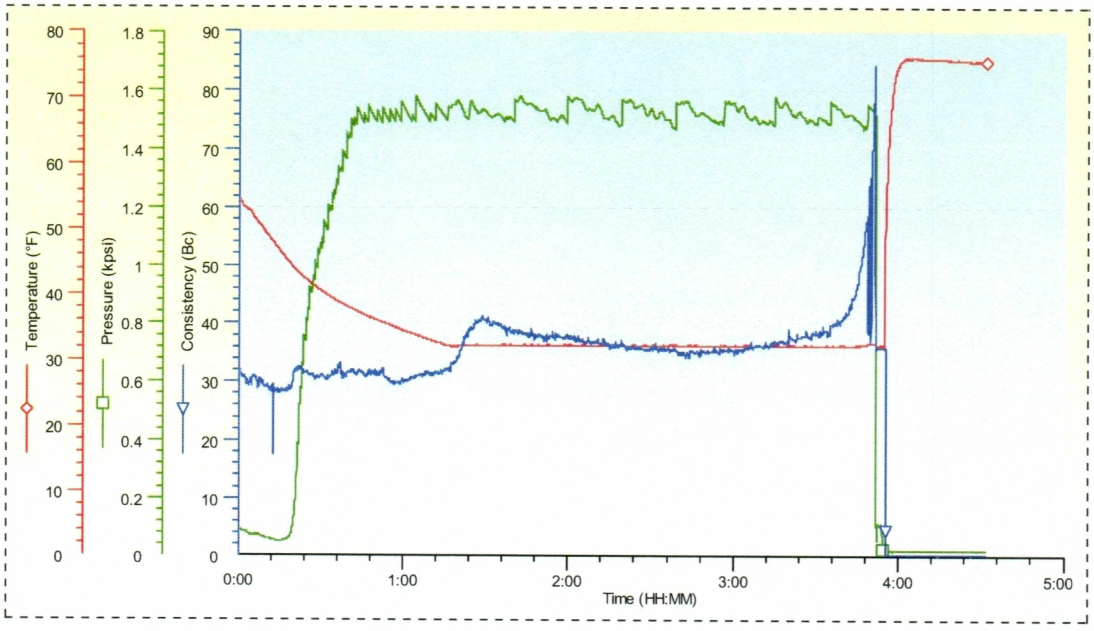


Figure 15: Consistometer run #2, 1500 psi and 32°F

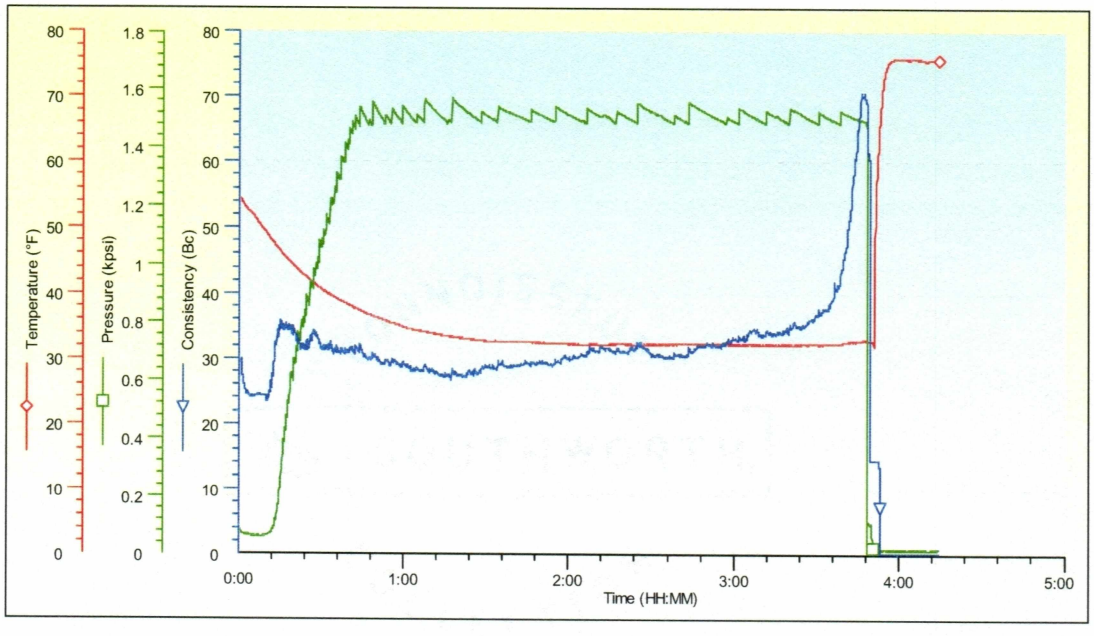


Figure 16: Consistometer run #3, 1500 psi and 32°F

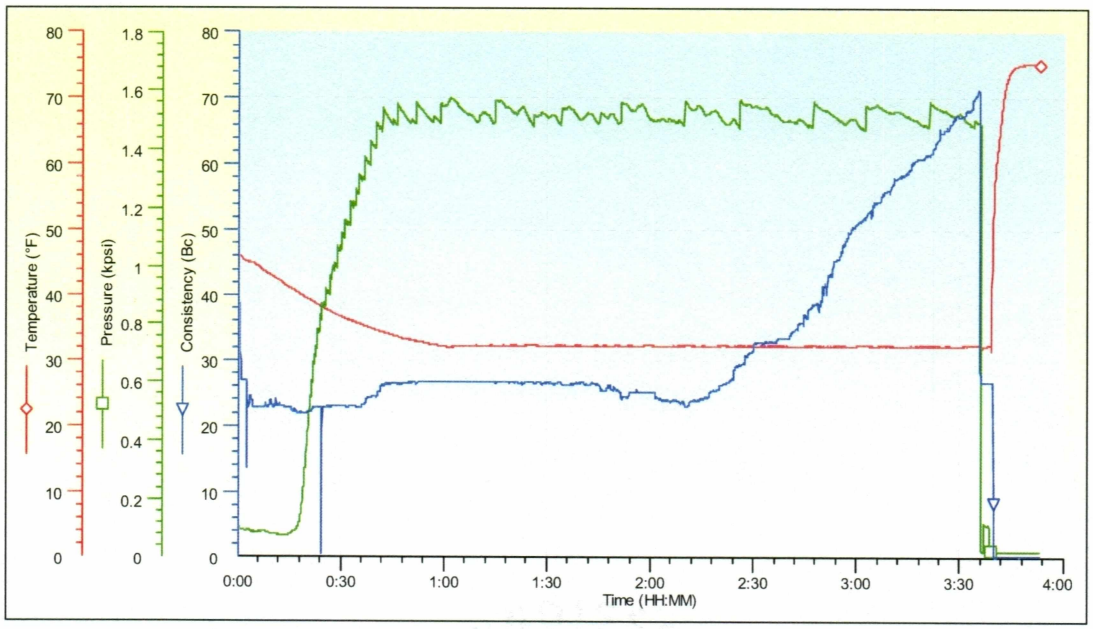


Figure 17: Consistometer run #4, 1500 psi and 32°F

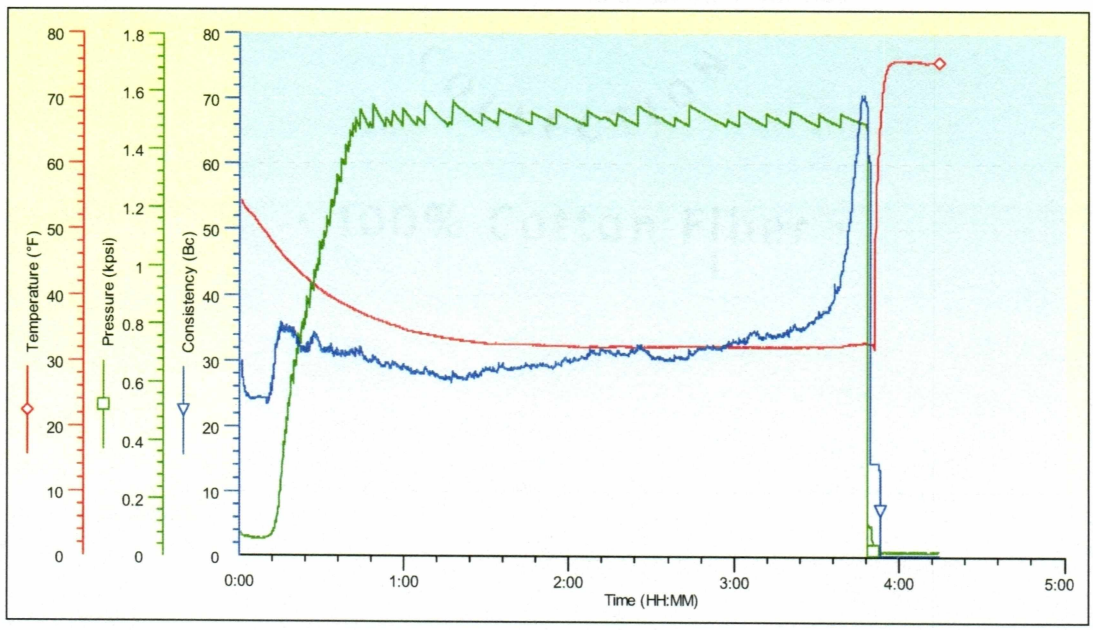


Figure 18: Consistometer run #5, 1500 psi and 32°F

As can be seen in the data from individual runs of the consistometer, even constant conditions will produce variations in pumping time as long as 45 minutes to an hour. It was also observed that the consistometer did not produce the smoothly changing behavior of an ideal consistometer test. An ideal consistometer test is shown in Figure 19. As can be seen, the rate of temperature and pressure change is constant and smooth with no significant fluctuations within the testing chamber. The behavior of the slurry is equally constant with a steady-linear period of consistency in the range of 10-30 Bearden units, before an exponential increase in consistency marks the limits of the slurry's pumpability.

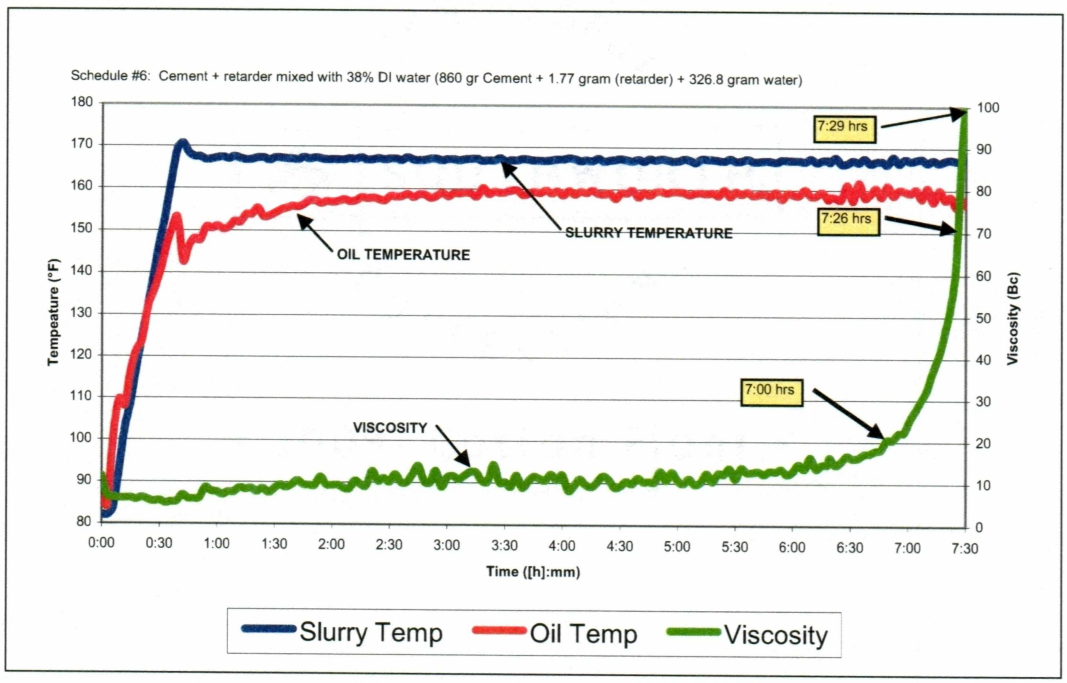


Figure 19: Illustration of ideal consistometer behavior, 3000 psi and 160°F

In Figures 14 through 18, the smoothness of this ideal behavior was not observed. Instead, the process control systems of the consistometer allows for fluctuations in the pressure and temperature desired. Furthermore, the consistency of the slurry does not always obey the linear-exponential relationship that is expected of a cement slurry, indicating either some unusual behavior within the slurry or unusual behavior in the data collection process.

Of these two options, it is more reasonable to assume that deviations are due to the data collection process. Should Ceramicrete have atypical consistometer behavior, some precision in the recorded data would exist between runs. Rather than the ideal behavior outlined in Figure 17, the individual run data would reveal a new trend for this novel material. However, no precision is seen in deviant data. Instead, the majority of data collected show trends mirroring ideal behavior with a small minority showing widely different behavior. In these runs, there is no reproduction of behavior but there was frequently doubt as to whether operator error had occurred.

Consistency measurements are highly dependent on the maintenance of the consistometer and on the calibration of the feedback mechanism by human operators. For data runs where the slurry exhibits consistency on the order of water, or shows unrealistically rapid increases in consistency, or both, there has likely been operator error

and the data should be discarded. Consistometer runs where the data-collection was in question can be observed in Appendix B.

However, even with the error propagated by the consistometer measurements themselves, the Ceramicrete slurry shows a pumping time that falls consistently in the middle of API specifications. This pumping time is highly adaptable, and can easily be adjusted by the operator by varying the percentage of boric acid retarder in the Ceramicrete blend.

5.2. Freeze Resistant Setting

As the source of most arctic cementing problems is premature freezing, Ceramicrete slurry was placed in cylindrical molds and allowed to set overnight at temperatures as low as 14° F.

At each temperature, identical behavior was observed. After 24 hours, each sample had set without any sign of freezing. After two hours at room temperature, no signs of thaw subsidence were observed. No ice was observed in the set product, nor did a visual inspection reveal any signs of increased porosity. These samples were later used in uniaxial compressive strength tests.

Table 4: Setting behavior at different temperatures

Temperature (°C)	Did the slurry successfully set?
20	Yes
15	Yes
10	Yes
5	Yes
0	Yes
-5	Yes
-10	Yes

Freezing is the single greatest problem experienced by Portland cement under arctic conditions and also the greatest hurdle for an alternative cementing system to overcome. In a temperature range reasonable for the permafrost areas of the Alaskan North Slope, Ceramicrete consistently sets with no sign of freezing and no need for external heating. Setting behavior is summarized in Table 4. In order for successful setting to occur, one need only keep the slurry water slightly above the point of freezing before blending with the dry Ceramicrete powder. During field operations, frequently this slurry water is heated well-above freezing, reaching temperatures as high as 80° F. Since Ceramicrete requires far less energy to be expended on keeping the slurry water unfrozen,

and requires no external heat once the reaction process actually begins, it provides significant advantage over current industry solutions.

In addition, one of the key binders (KH_2PO_4) serves as a natural freezing point depressant for slurry water, negating the need for additional additives. Gypsum cement blends, for example, make judicious use of various salts to depress the freezing point of water, increasing the overall cost of cementing operations. By removing these costs and additives, Ceramicrete proves a competitive alternative to current industry solutions for cold region cementing.

5.3. Thermal Conductivity Tests

Researchers at ANL documented that a period of two hours, fourteen minutes was required to raise the temperature of a chilled disk of Ceramicrete from a uniform 39.3° F to 68° F. Working under the effective assumption that heat transfer was radial in one-direction, the rate of heat transfer through the material was calculated as follows (Cengel, 2001):

$$\frac{T(t)-T_\infty}{T_i-T_\infty}=e^{-bt}=\frac{39.2999-68}{39.3-68}=e^{-b(43{,}860s)} \qquad 5.1$$

The value of 'b' was calculated to be $2.79*10^{-5}$ s^{-1}. Using this value, back calculate the coefficient of heat transfer, h using:

$$b = \frac{h}{\rho C_p L_c} \tag{5.2}$$

$$h = b\rho C_p L_c = (2.79*10^{-5})(0.27)(0.87)(0.0689) = 8\ W/m*k \tag{5.3}$$

where:

$$L_c = \frac{V}{A} = 0.0689 \tag{5.4}$$

To confirm this manner of calculating the heat coefficient, this value of 'h' was used to calculate the Biot number as follows:

$$Bi = \frac{hL_c}{k} = 0.89 \tag{5.5}$$

As the Biot number is greater than 0.1, one may see that the method used is appropriate as the sample does not exhibit lump system behavior. The final calculated value of heat transfer was 0.3 BTU/ft^2-°F.

The results of this test indicate that Ceramicrete maintains the desirable ceramic property of high insulation while still providing an equivalent heat of hydration to current industry solutions. A heat transfer value of 0.3 BTU/hr-ft-°F is 38.3% lower than that of a

gypsum-Portland blend, which transfers heat at a rate of 0.486 BTU/hr-ft-°F. This comparison is graphically presented in Figure 20.

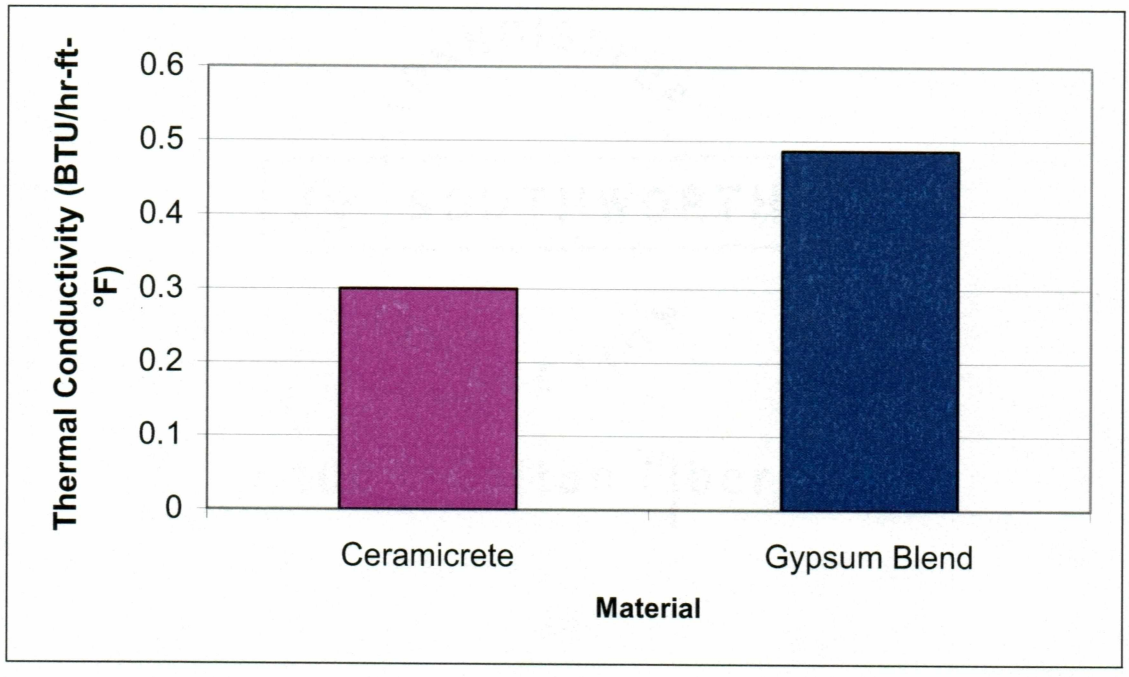


Figure 20: Comparison of thermal conductivities shows Ceramicrete to be more insulative than a gypsum blend

5.4. Heat of Hydration

Examining the reaction mechanism, literature values of the heat of formation for each component were also researched, and an analytical value of the heat of reaction for Ceramicrete was estimated. The mechanism of the Ceramicrete reaction has been established in previous work at ANL, as outlined in Chapter 3. Using this mechanism, as

well as values for heat of formation derived from the literature (Table 5), the heat of hydration is analytically determined to be 99.5 BTU/lbm.

Table 5: Enthalpies of formation of various Ceramicrete components (Wagh, 2004)

MgO	KH_2PO_4	H_2O	$MgKPO_4 \cdot 6H_2O$	ΔH	Units
-601.6	-1570	-285.8	-3724.3	-123	kJ/mole
-570.2	-1488.1	-270.9	-3530.1	-116.6	BTU/mole

A more accurate method to determine the heat of hydration would be the use of a bomb calorimeter. However, the heat of hydration is affected by a number of different variables, such as reaction temperature, free water fraction, etc. that are difficult to keep consistent during field operations. Thus, the more 'accurate' experimental method was abandoned in favor of an analytical method which would quickly and easily provide a reasonable estimate for the heat of hydration. The analytically-determined heat of hydration is on-par with that of most refractory permafrost cements, which frequently display heats of hydration in the range of 92-115 BTU/lbm. Thus, as illustrated in Figure 21, no advantage is seen in the use of the specialty Ceramicrete material in reducing the heat of hydration. This could perhaps be further modified through the use of dilutent additives, such as an increased fraction of fly ash in the final Ceramicrete blend. This

method has seen use in the development of calcium aluminate cements, which have a particularly high heat of hydration. A larger fly ash component in these blends mitigates the effect of this heat of hydration upon the surrounding formation by slowing the release of heat into the formation and diluting the reaction itself.

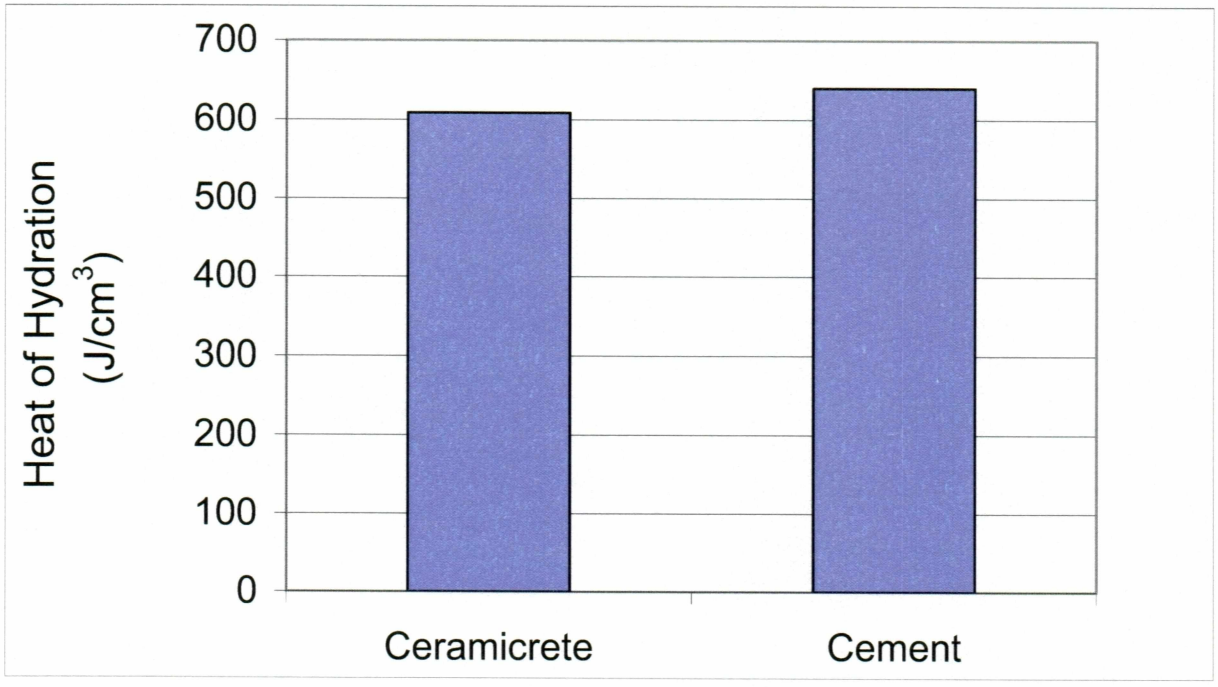


Figure 21: Heat of hydration for oilfield cements and Ceramicrete are equivalent

5.5. Reactivity to Hydrocarbons

In Figure 22, a Ceramicrete slurry was put through consistometer testing with embedded chunks of dry ice. The figure illustrates the dissolution of the dry ice into

carbon dioxide gas, both increasing the operating pressure of the run and exposing the slurry to a high-carbon environment during its thickening. Despite changes to the chemical environment, the slurry shows no noticeable deviation from the behavior illustrated earlier in this chapter, as the slurry neither remains viscous or thickens prematurely.

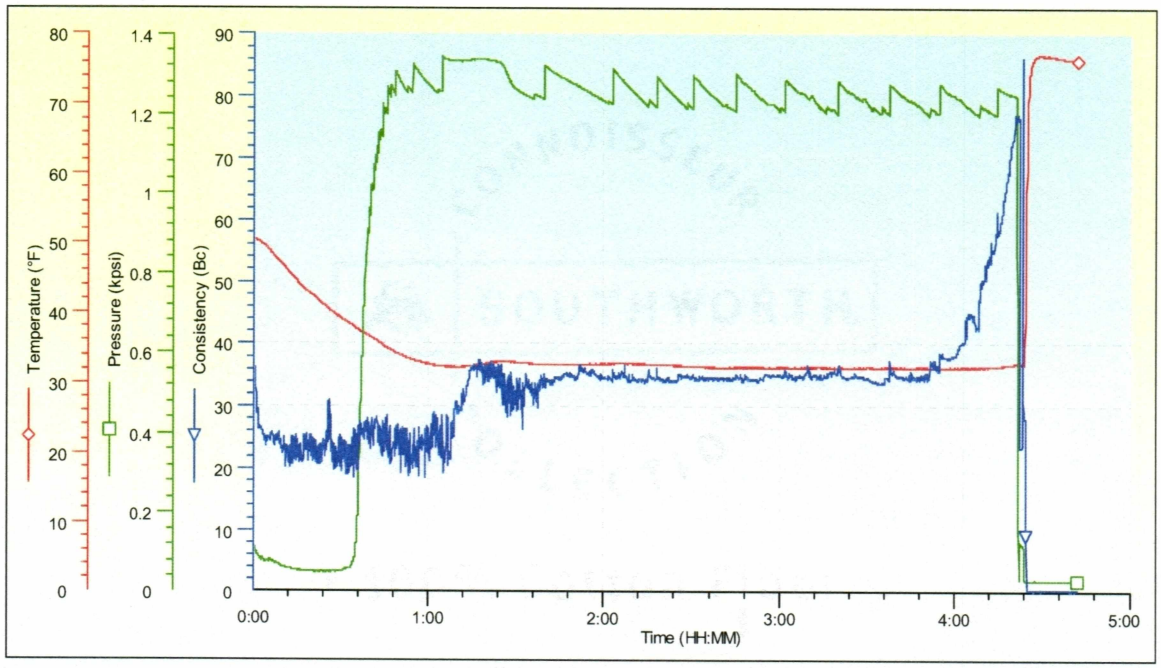


Figure 22: Consistometer run containing dry ice particles

Upon completion of the consistometer run, the tested slurry was poured into cylindrical molds and buried within additional dry ice before being placed in a refrigerated environment. The resulting samples were found to have set properly 24-hours later, despite the carbon-rich environment. There were no signs of premature freezing,

degredation of the ceramicrete product, or signs of increased porosity after visual inspection.

The use of dry ice in this test was valuable for a number of different reasons. First, it provided a ready source of carbon that was easily sublimated into a slurry or to surround a mold containing Ceramicrete. It is easier and cheaper to work with than crude oil, while adequately simulating the chemical effects of a hydrocarbon environment.

Additionally, carbon dioxide is a common element in downhole gases. Thus, it is valuable to understand how Ceramicrete will react in a carbon dioxide-rich environment. This is currently an industry-concern with conventional permafrost cement formulations, which have shown themselves to flash set in the presence of carbon dioxide gas. As Ceramicrete shows itself to be chemically neutral in this environment, it becomes an advantageous material to use in areas that have been previously exposed to a carbon dioxide sweep, areas with carbon dioxide entrapping gas hydrates, or in areas where carbon dioxide sequestration may occur.

5.6. Reactivity to Portland Cement

Figures 23 through 25 are consistometer-runs in which the Ceramicrete blend contained significant proportions of Portland cement granules. Though the percentage of Portland cement impurities increased up to 30% by weight of the Ceramicrete blend, no

significant changes were observed in the consistometer data to indicate that the impurities were affecting the pumping time of the slurry.

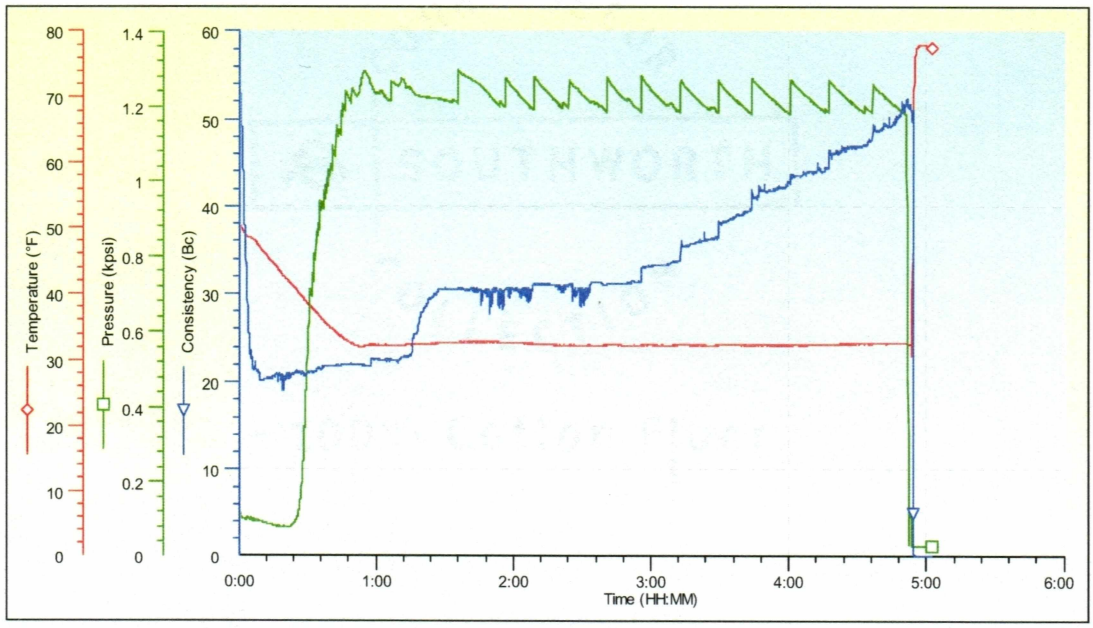


Figure 23: Consistometer run, 10% Portland cement granules

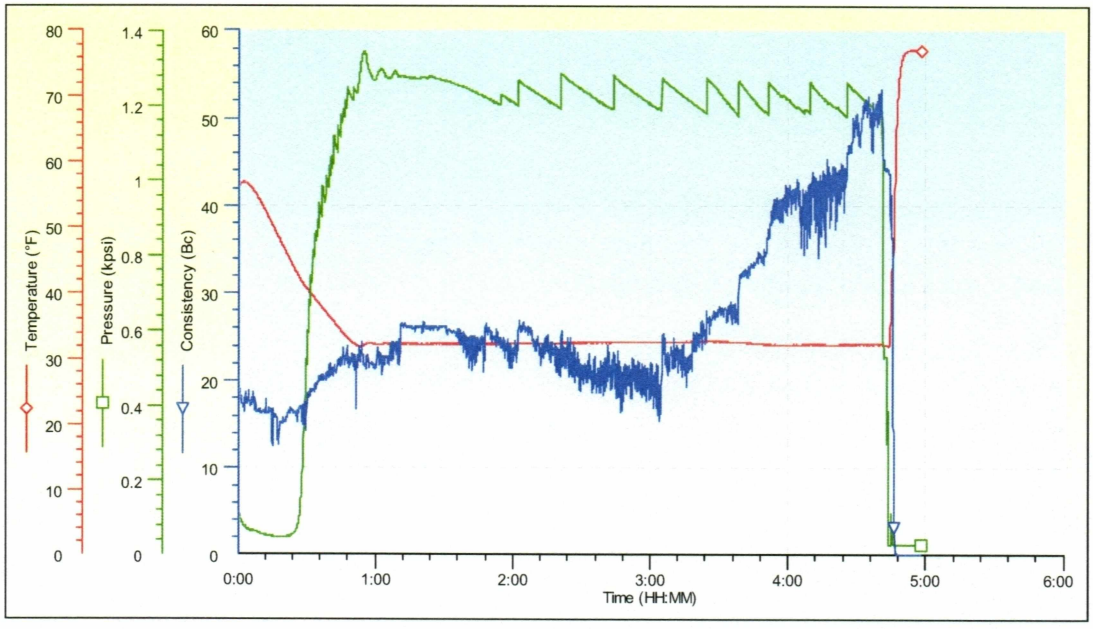


Figure 24: Consistometer run, 20% Portland cement granules

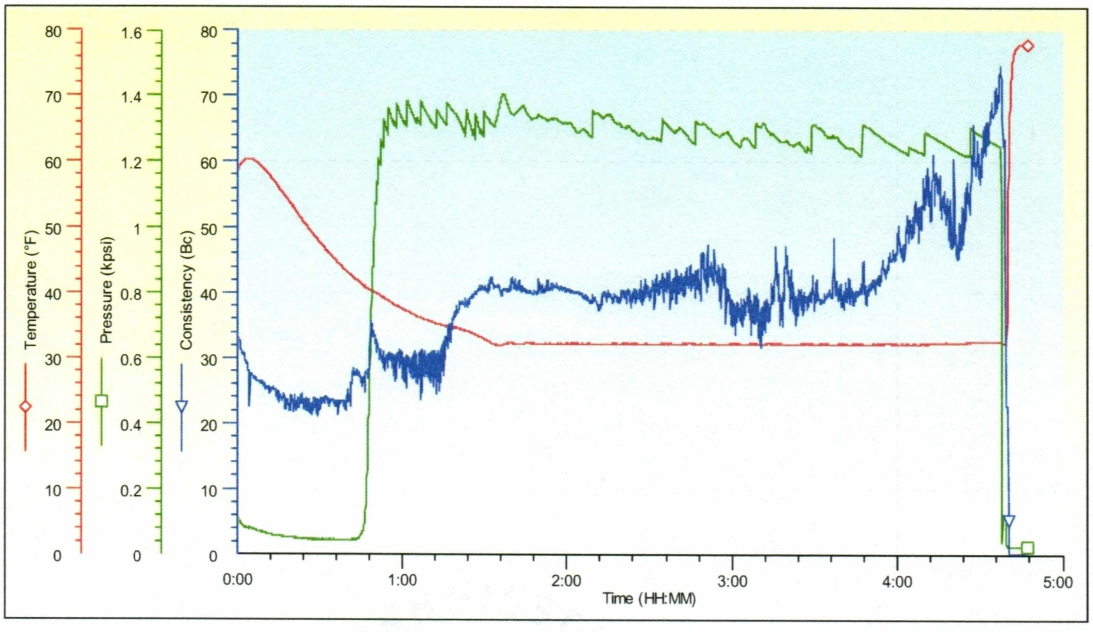


Figure 25: Consistometer run, 30% Portland cement granules

The slurries from these consistometer runs were cast into cylindrical molds and allowed to set at 36.2° F for 24 hours at the facilities at ANL. A visual inspection after this time showed no signs of freezing, no signs of flash setting, no signs of increased porosity, or other signs of changed setting behavior. Upon transport to the facilities at the University of Alaska Fairbanks, these samples were tested under uniaxial compression. These tests showed that Portland cement impurities had no effect on the final setting strength of the Ceramicrete product.

However, as unreacted Portland cement powder is as likely to be a field impurity as granules of set Portland cement, additional tests were performed by adding varying amounts of Portland cement powder to the Ceramicrete blend. Though no consistometer data is available for these impurity tests, uniaxial testing was performed after the mixed Ceramicrete slurry was allowed to set for 24 hours at 36.2° F. Representative compression data can be observed below in Figures 26 and 27.

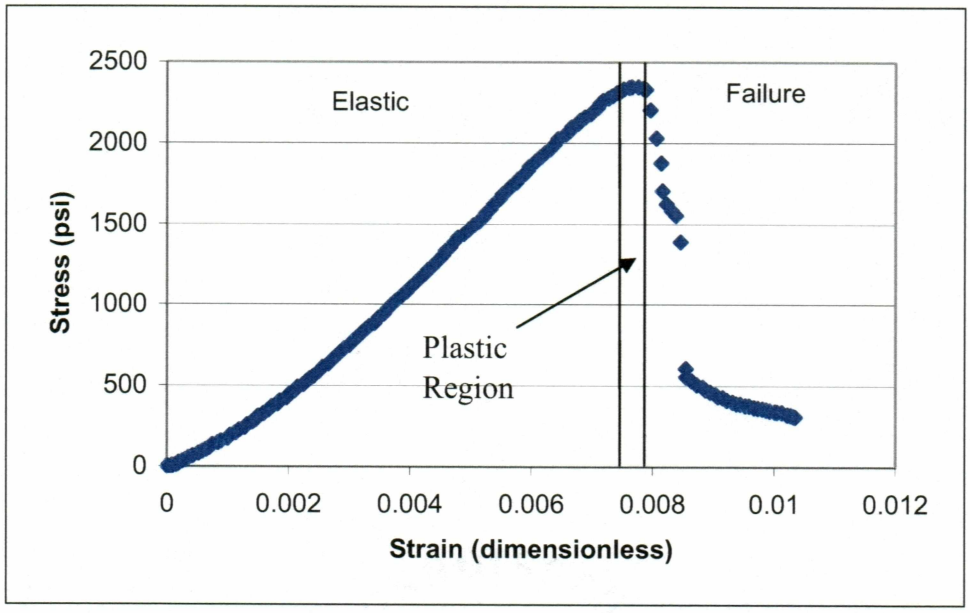


Figure 26: Compression data, 10% Portland cement powder

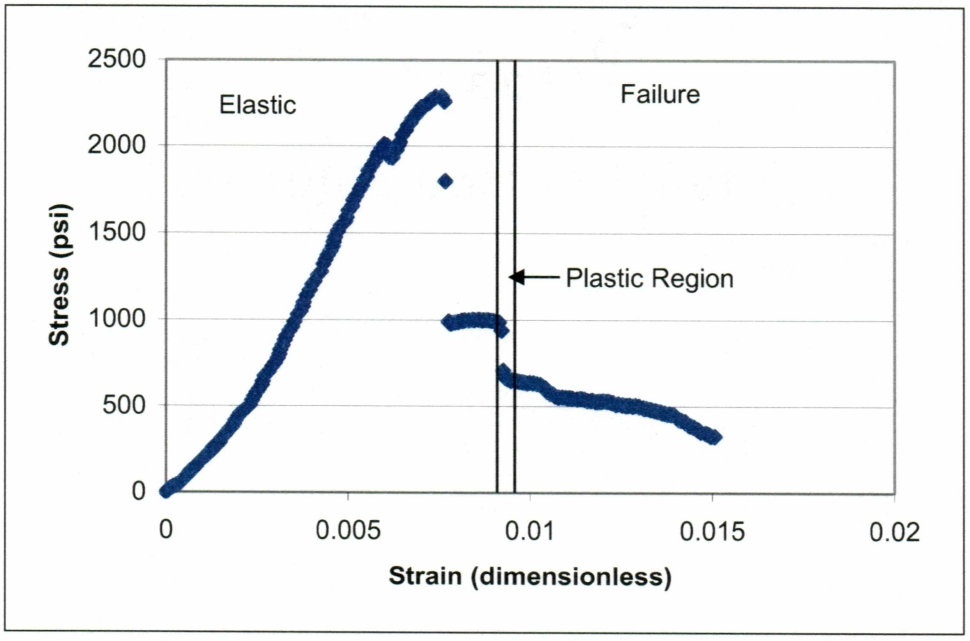


Figure 27: Compression data, 30% Portland cement powder

The ultimate compressive strength before failure shows very little dependence on the degree of Portland cement impurity that exists within the Ceramicrete slurry. Consistently, a compressive strength of 2200-2600 psi is observed in samples prepared with these impurities, which is inline with the behavior of a pure Ceramicrete product.

As outlined in Chapter 2, adverse reactions to conventional Portland cement have been a primary drawback of other permafrost cementing solutions, namely the calcium aluminate family of cements. This drawback has been the major driving force behind the investigation and adoption of gypsum cement blends, as the cost and inconvenience of flash setting has negated much of the usefulness of calcium aluminate cements. If Ceramicrete had equally adverse reactions to conventional cement materials, its use as a specialty engineered material would have likewise decreased.

However, all available results indicate that the presence of Portland cement, in a pre- or post-set state, has no effect upon the setting behavior or strength of the final Ceramicrete product. The components of Portland cement do not contribute in any significant way to the reaction mechanism of Ceramicrete, nor do they appear to generate any unwanted competing reactions during the acid-base generation of the ceramic product. In this fashion, it already exceeds the calcium aluminate family of cements as a solution to the problem of cementing in low temperature environments.

5.7. Slurry pH

In the development of a chemically-unreactive slurry, it is desirable to have pH neutrality, particularly in a material that is generated via an acid-base reaction. To test this, pH measurements of Ceramicrete slurries were measured after each and every successful consistometer run. A histogram of the collected data in Figure 28 illustrates the distribution of measured slurry pH.

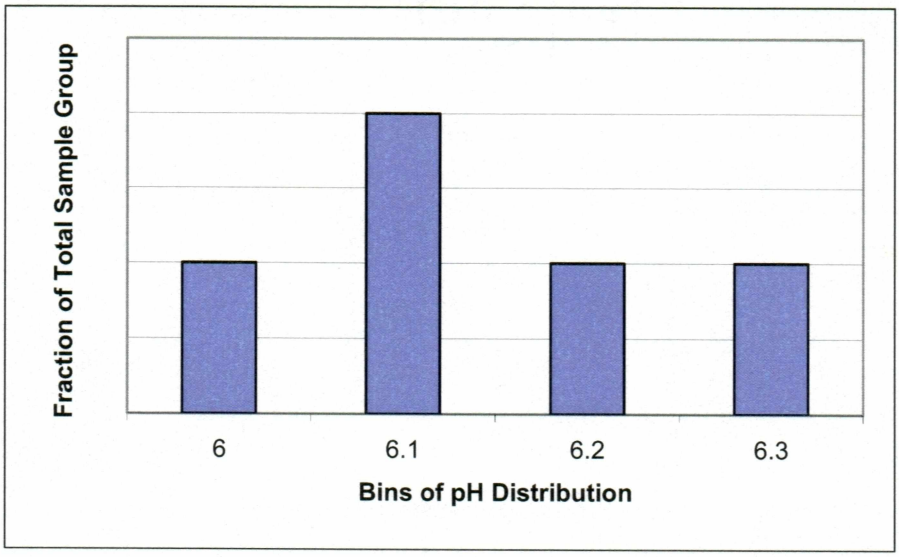


Figure 28: Distribution of slurry pH

Despite dependency on an acidic environment to initially drive the production of a ceramic product, Ceramicrete generates a surprisingly neutral slurry at the end of its thickening time. The slurry has a pH of about 6.1, with a small range of deviation. To provide a sense of scope, the final Ceramicrete slurry is less acidic than human saliva,

showing comparable acidity to 'soft' tap water. The slurry, including the weak acid dihydrogen phosphate ion, serves as a chemical buffer to any strong bases or acids it may encounter downhole. This buffering effect helps ensure that the Ceramicrete setting reaction is not disrupted by downhole proton donors or acceptors, which might otherwise upset the reaction mechanism.

5.8. Slurry Density

In filling a bulbed pipette known to have a volume of one cubic centimeter with Ceramicrete slurry, an observed mass change of 1.9 grams was apparent. As such, slurry density was easily calculated to be 1.9 g/ml or 1.9 g/cm^3.

Ceramicrete shows very little expansion during the setting process, so measurements of slurry density are effective tools for measurements of the density of the final set product. In this case, the permafrost formulation of Ceramicrete exhibits a less dense set product than a corresponding Portland cement. With an increase of 20%, Portland cements have a density on the order of 2.25 grams/cm^3, as in Figure 29.

Despite a lower density, there is a decrease in interstitial spacing in Ceramicrete relative to Portland cement. As outlined in the chapter one, one of the primary problems in arctic cementing is the presence of these porous spaces. As water or other fluids fill these spaces, freezing temperatures lead to expansion of the fluids and cracking of the set

product. By reducing the void spaces in the set product, one avoids potential invasion by fluid and the subsequent damage that occurs in sub-freezing temperatures.

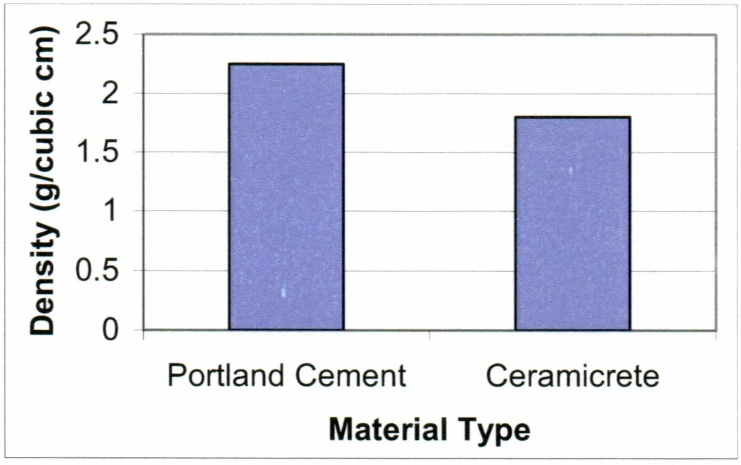


Figure 29: Relative density of Ceramicrete and Portland cement

5.9. Connective Porosity Measurements

A 708 gm cylinder of set Ceramicrete was submerged in water for a period of 24 hours. After this period of time, it was removed from its water bath, shaken dry, and its mass was remeasured. After an extended submergence, the cylinder showed a gain of 0.7 gm, less than 0.1 percent of the original mass.

Presuming a density of 1 gm/cm^3 for pure water, this corresponds to an open porosity volume of 0.7 cm^3. As the cylindrical molds have a volume of 205.92 cm^3, this indicates that open porous space composes roughly 0.3% of the total volume.

Open porous spaces become important in two regards. The first, outlined in the introduction and again in regards to density measurements, is in the avoidance of fluid invasion into the set product. As has been repeatedly discussed, open porous space allows for fluid entry. As temperatures drop, this fluid freezes and expands, straining and cracking the final set product. These microfractures significantly decrease fatigue resistance in the set casing, contributing to a shortened product lifespan and the need for frequent repair work upon the casing itself.

The second concern that arises with large open porous spaces is in terms of permeability. A casing shoe must not show a high permeability for fear that the oil and gas produced in a well will find passageways through which they can migrate into the surrounding formation. This is both damaging to the environment and costly to the field operator as lost production. Portland cement, by comparison, is composed of 5% by volume open space, a factor of 10 times more susceptible to oil and gas migration than its Ceramicrete counterpart. This is illustrated in the pie charts of Figure 30.

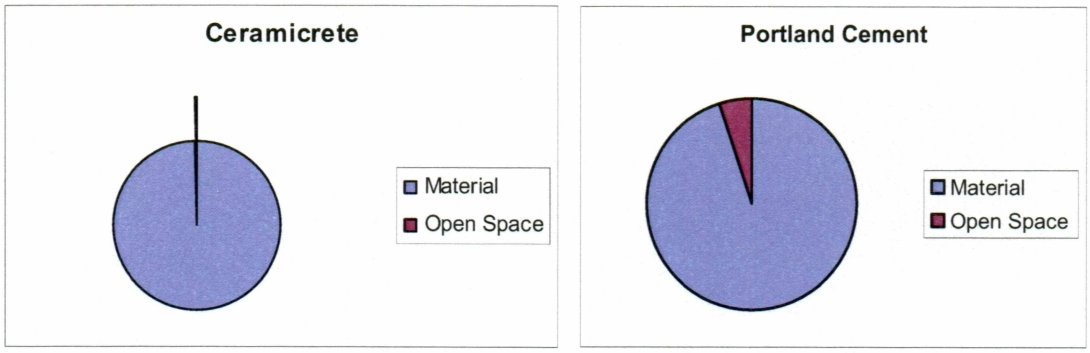


Figure 30: Open porous space in Ceramicrete and Portland cement

5.10. Rheology Measurements

Rheology is the science and study of the deformation and flow of matter. Rheology is an extremely important property of drilling muds, drill-in fluids, workover and completion fluids, cements and specialty fluids and pills. Fluids are described as Newtonian or non-Newtonian depending on their response to shearing. Shear stress of a Newtonian fluid is proportional to the shear rate. Most fluids used in oilfield operations are non-Newtonian fluids, with viscosity decreasing as shear rate increases, and correspond more closely to one of the other three models shown in Figure 31.

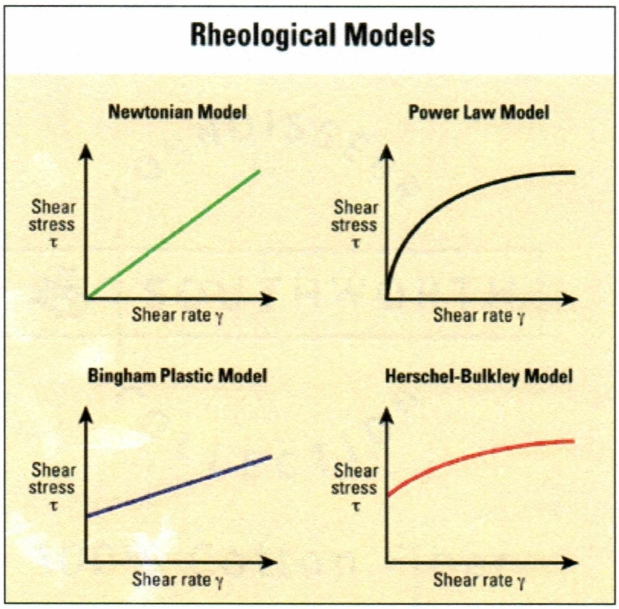


Figure 31: Different rheological models used to describe oilfield fluids

(Schlumberger, 2005)

In the case of cement, two models are predominantly used to characterize its viscous behavior: the Bingham plastic model and the power-law fluid model. This study used only the power-law model which describes the relationship between the shear stress and shear rate of cement as an exponential relationship (Schlumberger, 2005):

$$\tau = k(\gamma)^n \qquad 5.6$$

Figure 32 is a rheogram of Ceramicrete slurry behavior at room temperature and atmospheric conditions. All testing was performed according to API specifications on an Ofite 900 rheometer. With an r-squared value of 0.94, a power law model was applied to

the rheometer data. Using regression analysis in EXCEL, a consistency value ('k') of 90.7 was established as well as a power-exponent of 0.239.

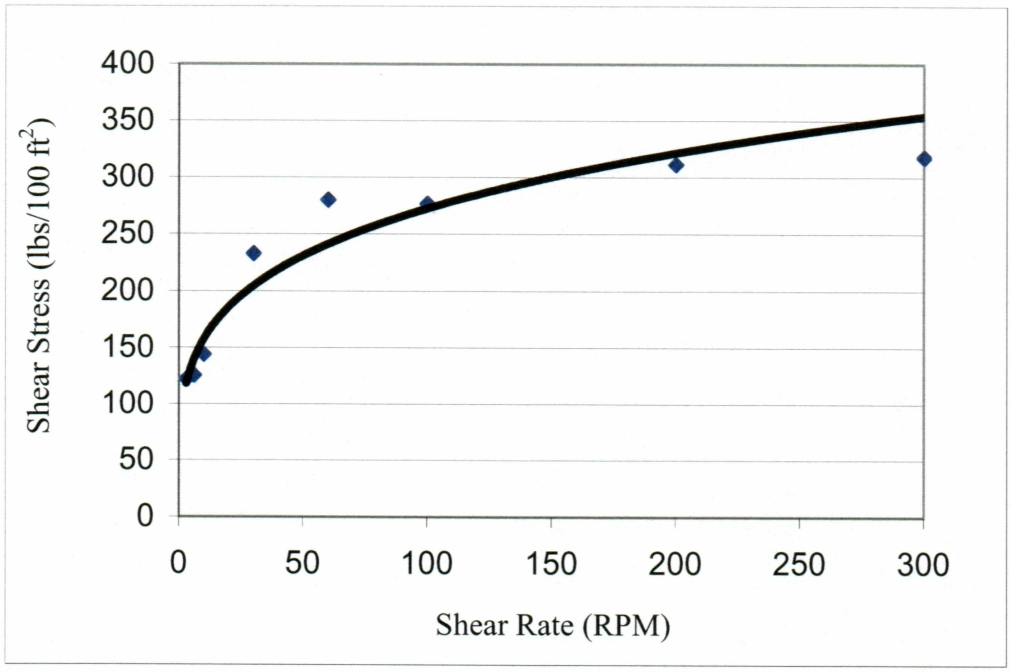


Figure 32: Rheogram for Ceramicrete at room temperature

Rheology measurements of the Ceramicrete slurry are interesting in that they illustrate behavior that is both like and unlike that of conventional cements. In terms of the slurry's response to shear stress, Ceramicrete demonstrates an exponential curve similar to that of API Class C or Class H cement. A listing of average rheological measurements for different classes of API cement is provided in Table 6. However, though the curve development is similar, the consistency value from these experimental trials is two orders of magnitude greater than what would be expected of oilfield cement;

where Portland cement slurry would be water-like in consistency, Ceramicrete quickly thickens into a paste-like gel. This difference in initial consistency can best be illustrated through the use of a log-log plot that represents the relationship between shear stress and shear rate. Rearrange the power-law model as follows to obtain such a log-log relationship:

$$\log \tau = \log (k\gamma^n) \tag{5.7}$$

$$\log \tau = \log k + \log \gamma^n \tag{5.8}$$

$$\log \tau = \log k + n \log \gamma \tag{5.9}$$

Using the relationship in Equation 5.9, as well as the values listed in Table 6, a more direct comparison between Ceramicrete and API cements can be seen in Figure 33.

In Figure 33, it becomes apparent that while Ceramicrete has a similar value for its power exponent (illustrated by a near-identical slope to those of API cements), the initial consistency of the slurry is vastly different, as seen by a significantly larger y-intercept. This would be of greater concern if the consistency of Ceramicrete were not so readily adaptable; all rheology tests were performed upon a blend of Ceramicrete that did not contain any boric acid retarder. As such, gel formation and ceramic product proceeded almost immediately. The forming lattice network is far more resistant to sheer stresses than a cement slurry would be, resulting in the exceptionally high value for 'k'.

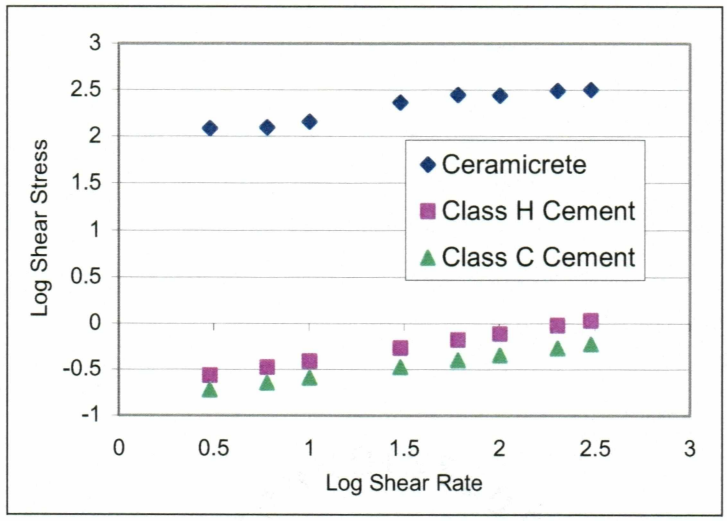


Figure 33: Log-log relationship comparing rheology of Ceramicrete to API cements

Table 6: Common rheology measurements for API cements (Smith, 1986)

API Cement Slurry	N	K
Class H	0.30	0.1950
Class C	0.25	0.1441
Class E	0.50	0.0472
Class G + 4% gel	0.10	0.9500

Yet by modifying the amount of boric acid in the Ceramicrete powder blend, a cementing operator can easily adjust the rate at which this lattice network forms. Should a more cement-like consistency be desired early on, addition of 0.1% by weight boric

acid should meet that requirement. Should thicker 'cement' be desired for squeeze jobs or to deal with situations of lost circulation, the boric acid can be omitted to have a better formulation for the task at hand.

By having an adaptable rheology, Ceramicrete allows the operator to have control over a number of other variables within the cementing operation. Use of rheological parameters allows for the determination of the annular velocity/pumping requirements necessary for laminar, plug, or turbulent flow. Furthermore, these parameters allow for the determination of the frictional pressure of the slurry within the pipe and annulus as well as the hydraulic horsepower necessary at the wellhead. Finally, rheology measurements factor into the necessary slurry volume required for a given contact time. By having adjustable rheological properties, Ceramicrete allows for a greater degree of control for the oilfield operator.

5.11. Uniaxial Compressive Testing

The results of the uniaxial compression tests depend greatly upon the method of sample production used. Using non-API approved methods, Ceramicrete samples were produced by mixing the powder blend with water in a desktop mixer. Samples produced in this manner showed an ultimate compressive strength of 800 to 1500 psi before failure. Degradation of strength was observed in these tests, as shown in Figure 34. Samples that were allowed to set at colder temperatures showed a consistently lower ultimate strength.

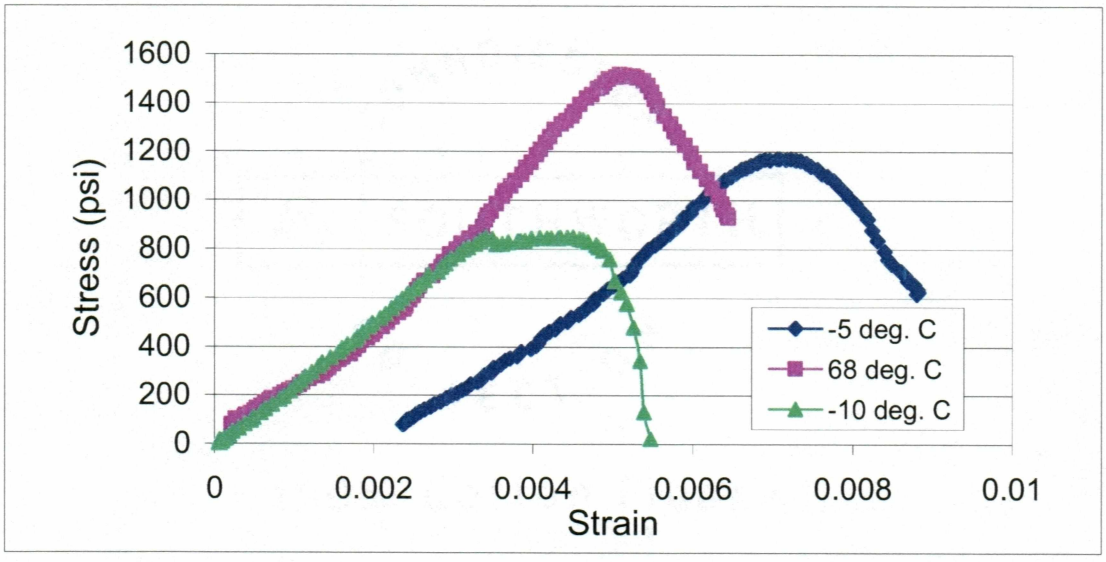


Figure 34: Compression testing data for desktop-prepared samples

Samples produced in an API-approved manner had a significantly higher compressive strength before failure. In these samples, the ultimate strength before failure exhibited a range of 2200-3000 psi, twice that of the desktop produced samples. Temperature-degradation of strength was also observed in this data set, with temperature being proportional to strength. This is illustrated in Figure 35.

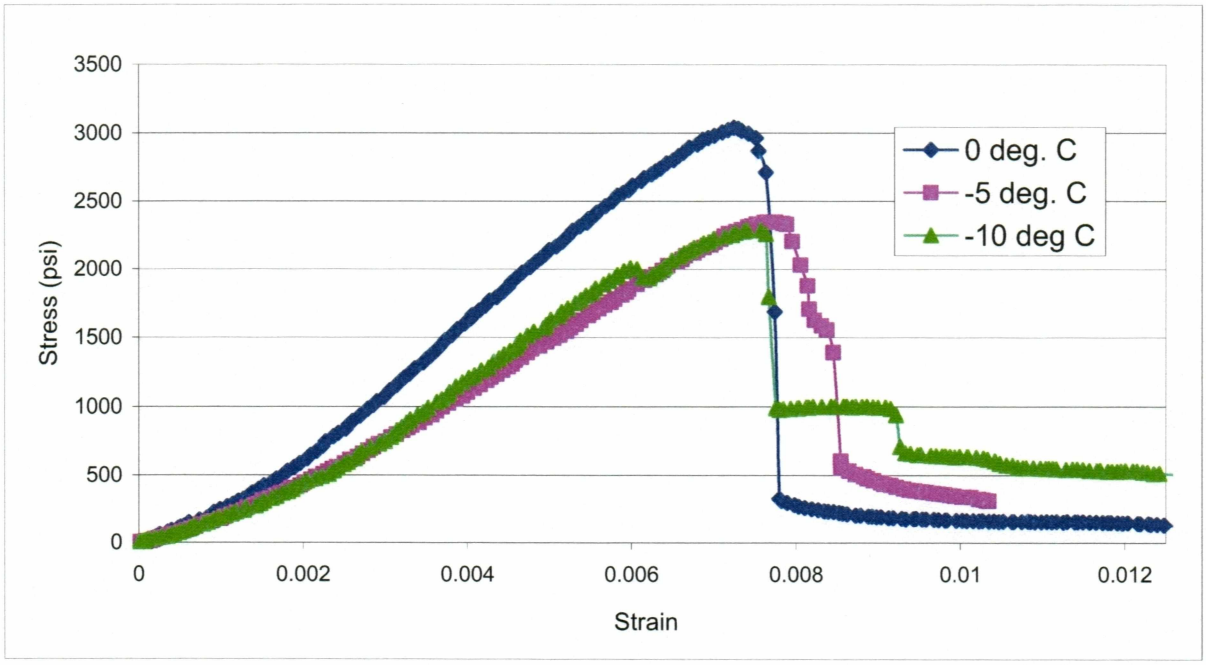


Figure 35: Compression testing data for API method of sample preparation

Another observable trend is the increase in plastic deformation in desktop-prepared samples over their consistometer-prepared counterparts. These samples showed significantly less brittle behavior, despite having a smaller Young's modulus of elasticity. Figures 36 and 37 demonstrate the compression data of samples produced by the desktop method, while Figures 38 through 39 are graphs produced for samples prepared in a consistometer. It can be seen that the first two graphs have a greater plastic region than their consistometer counterparts.

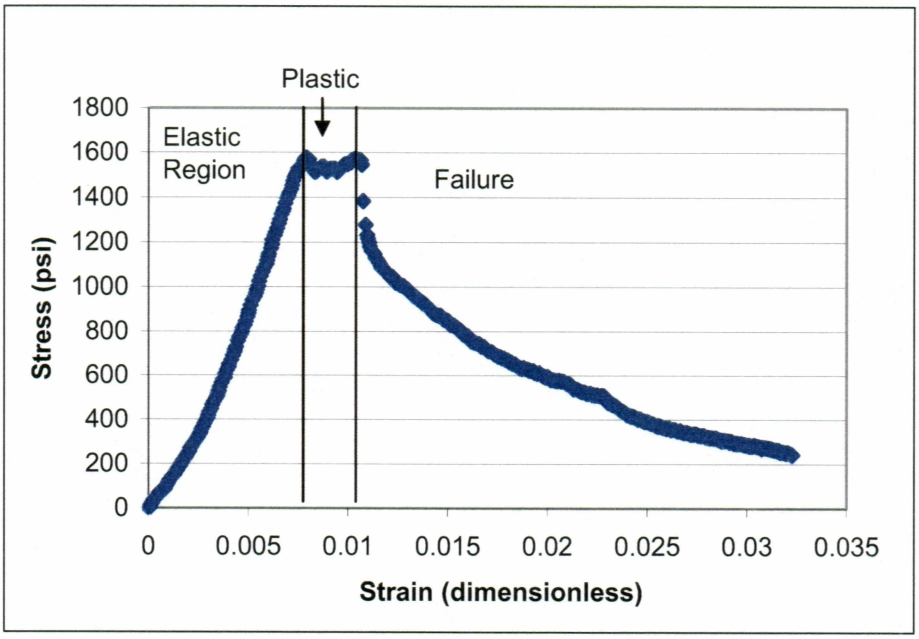


Figure 36: A representative graph of tabletop mixed compression data

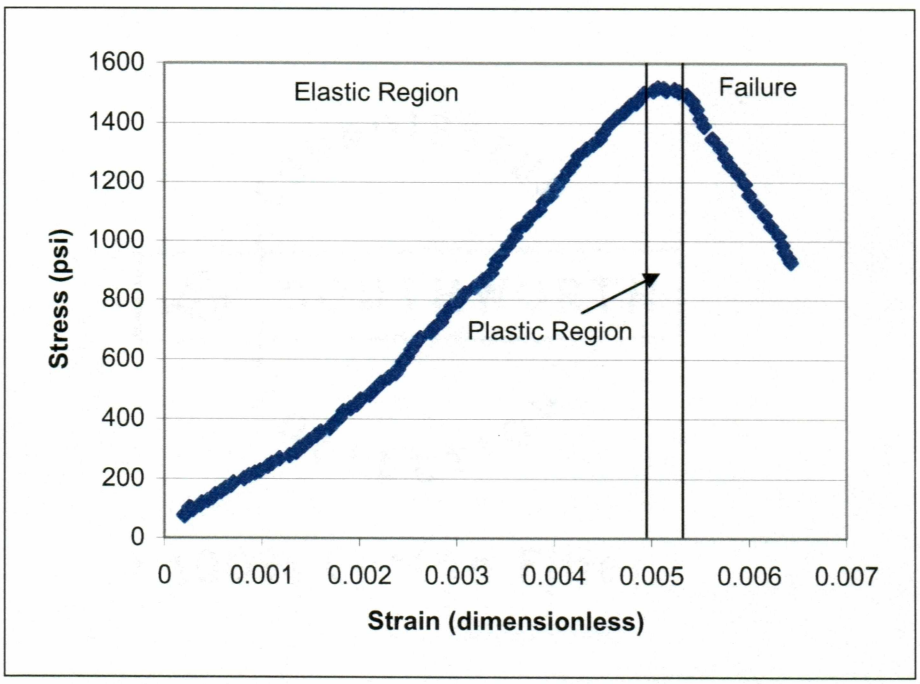


Figure 37: A second representative graph of tabletop compression data

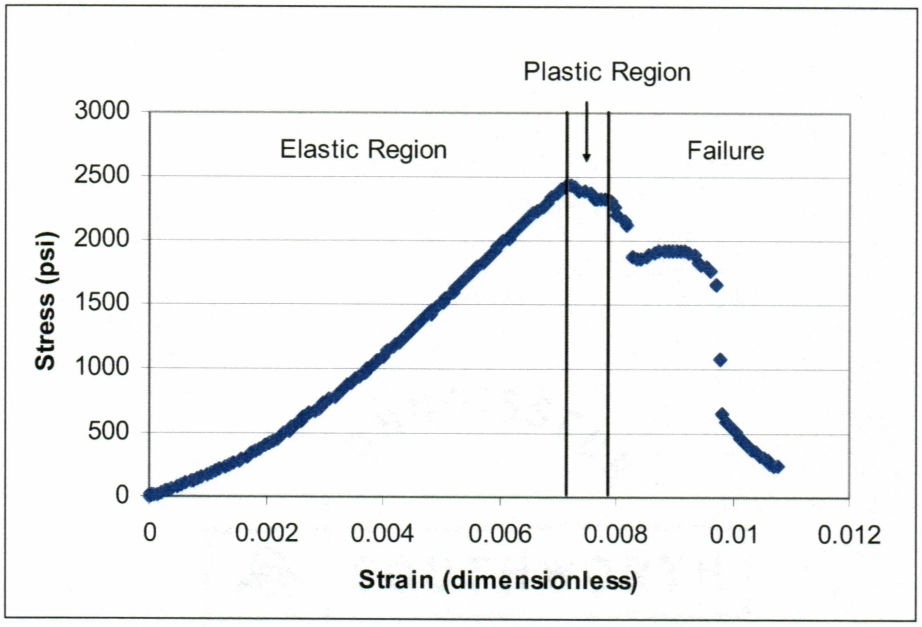


Figure 38: Compression data for Consistometer-prepared sample

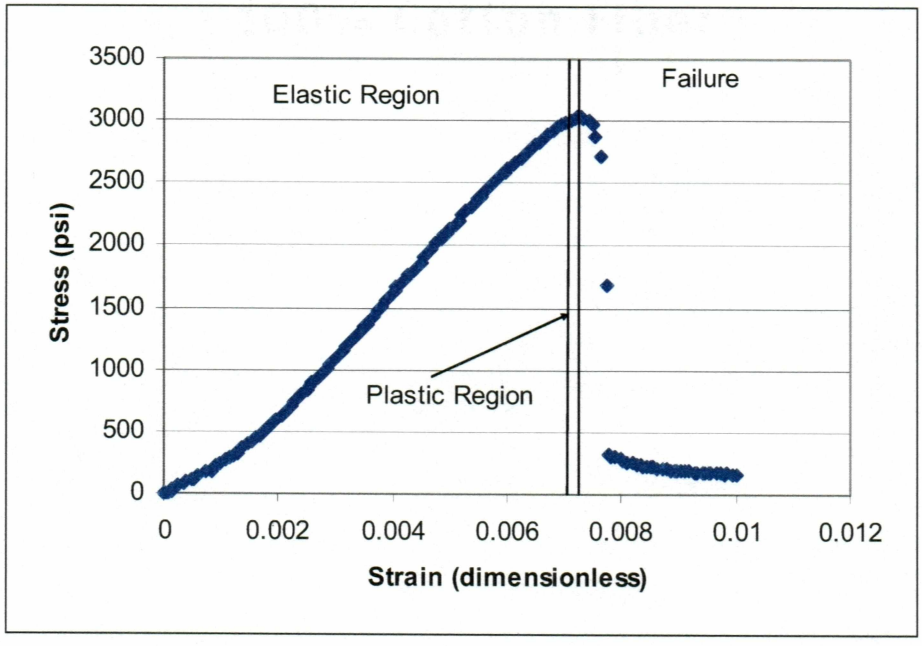


Figure 39: A second representative graph of compression data (consistometer-prepared)

In an attempt to establish a relationship between compressive strength and setting temperature, the data from these two production techniques were combined and averaged to create the figure below (Figure 40).

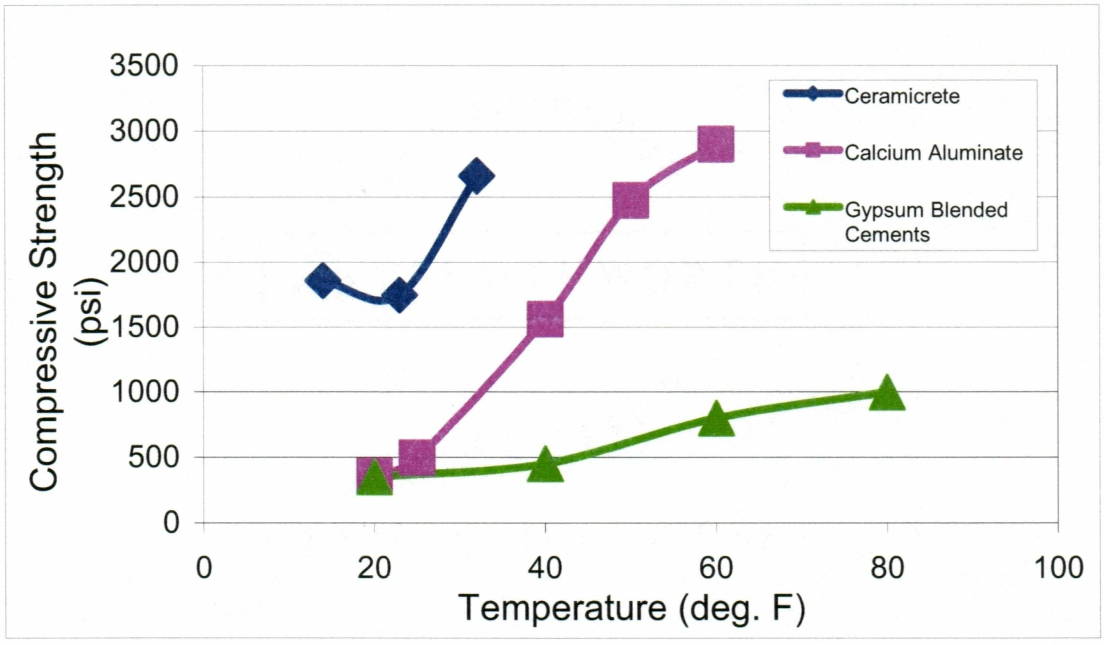


Figure 40: Temperature-dependent strength behavior for Ceramicrete and other cold-temperature cementing solutions

Though a clear relationship between strength and setting temperature cannot be determined from the sample group tested in the scope of this research, appearances certainly lend credence to the belief that lower temperatures result in a weaker final product, though the effect is neither abrupt nor great. Compared to the strength

development of gypsum cement blends and calcium aluminate cements, Ceramicrete shows more than competitive freezing behavior, with strength measurements thousands of psi greater than current industry solutions at low temperatures.

More interesting is the change in material behavior due to mixing method. An API approved consistometer method is reflective of oilfield measures, and assures a high degree of mixing in the cement slurry. This is particularly advantageous in the setting reaction of Ceramicrete, which requires mixing to ensure contact between the metal oxides and the aquasols within the reaction solution. Thus, in the consistometer-prepared samples, a strong lattice structure is assured and a high strength product develops that has all the brittle characteristics of a true ceramic.

In the desktop mixing method, however, there is no assurance of proper mixing of the Ceramicrete components within the slurry. Isolated sol groups are less likely to come in contact with each other and bond into ceramic chains, and the metal oxides are less uniformly dispersed within the slurry, leading to localized areas with high concentrations of nucleation points for ceramic generation. The end result, in theory, is a series of separate and overlapping lattice structures rather than one bound lattice structure. This both reduces the strength of the set product as well as increases its acceptance of plastic deformation without failure.

5.12. Splitting Tensile Strength Testing

Tensile strength testing is growing in prominence as a way of establishing material properties. This is due to a noticeable trend in cement-like materials, for which the behavior of the material under tensile stress simulates the behavior of the material under compression, but with a significantly reduced ultimate strength before failure.

For Portland cement, tensile strength is generally on the order of 1/4 to 1/8 the observed strength under compression. Using the STS method, Ceramicrete is demonstrating tensile strength on the order of 1/3 of its ultimate compressive strength. The material has operated in the range of 700-880 psi of strength when exposed to indirect tensile strength. A comparison is shown in Figure 41.

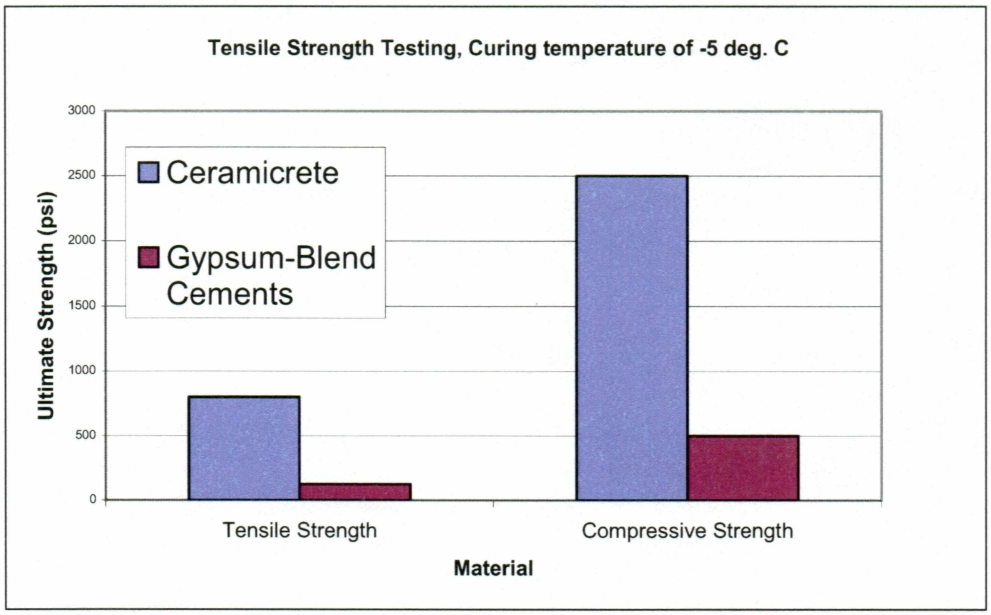
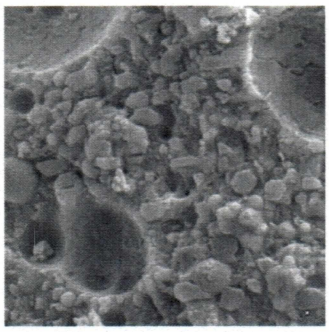


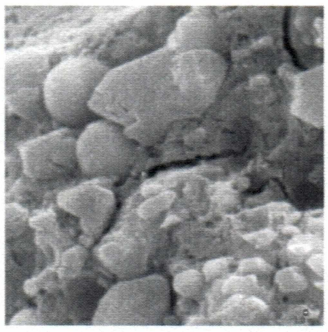
Figure 41: Comparison of tensile and compressive strength measurements

5.13. Scanning Electron Microscopy

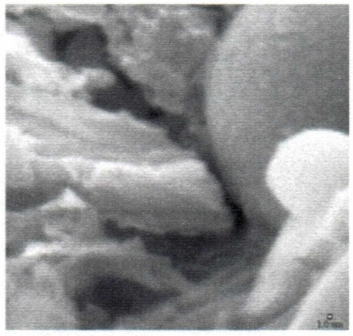
Under magnifications of 1500x or greater, certain generalizations can be made of the Ceramicrete product. First, its lattice structure appears highly crystalline, as expected. Oxide particle surfaces appear smooth, with striations indicating crystalline structure. The material shows a defined morphology, in comparison to Portland cement, which is amorphous and resembles glass in structure. This trend can be seen in the analysis of Figure 42.



Ceramicrete, 3800x



Ceramicrete, 6300x



Ceramicrete, 14000x

Figure 42: SEM photos depicting the structure of Ceramicrete at different magnifications

The dense, crystalline structure of Ceramicrete shows no void spaces indicating the former presence of ice crystals. Porous spaces, in general, appear absent and cracks in the structure appear only at higher magnifications (5000x or higher). Microfractures appear no more frequently in products set at colder temperatures than those set at room temperature, further indicating that there is no significant damage in the material due to freezing or cold temperature setting.

Chapter 6:

6.0. Conclusions and Recommendations

6.1. Conclusions

Reviewing the criteria for an ideal arctic cement, it becomes clear that Ceramicrete is a far more ideal solution than either Portland cement or current industry solutions. Ceramicrete demonstrates that it has overcome the temperature limitations that currently hinder Portland cement. Not only can Ceramicrete easily set without freezing in the range of temperatures that exist on the Alaska North Slope, but the material avoids the complications of high porosity, low compressive and tensile strength, and high permeability of Portland cement.

Compared to current specialty cements, Ceramicrete demonstrates a greater compressive strength at equivalent temperatures. It does not flash set or show reduced strength in the presence of Portland cement impurities, nor does it show an apparent reactivity with the chemical environment it is likely to encounter downhole. The heat of hydration for Ceramicrete is equivalent to that of other oilfield cements, but there is no need for the addition of freeze-depressants or external heat for the successful setting of Ceramicrete.

The material requires no new capital equipment or operator training for its use in the field, but still meets API specifications in regard to pumping and working time. Furthermore, its novel chemistry indicates that the material is much more adaptable than Portland cement, requiring only a minor modification in the amount of retarder added to the Ceramicrete blend to adapt its properties. The only conclusion that can be drawn from this research is that Ceramicrete provides a novel and highly advantageous arctic cementing solution.

6.2. Recommendations for Further Research

Additional research is still needed to develop strong characterizations of Ceramicrete. A fluid-loss program should be started to establish the ideal fraction of water that should be introduced into a Ceramicrete slurry. Furthermore, additional tests for wellhole compatibility should be performed, examining how various cement additives and downhole non-hydrocarbon chemicals may interact with Ceramicrete. Drilling fluids are of particular concern.

Should the equipment ever become available, it is also useful to examine the strength development of Ceramicrete using an ultrasonic slurry testing device. This provides a more accurate measure of the WOC time than is covered in the scope of this research. Another direction for further research may be to determine the exact relationship between the boric acid retarder and pumping time, as this relationship is not

quantitatively analyzed within the scope of this research. Finally, issues of engineering economics were not addressed in this study as cost was considered outside the scope of experimentation. However, as price is a major driver in the adoption of new technology, a study of Ceramicrete's cost effectiveness would be a useful investment of time and resources.

References

"Alaska Code 20 AAC 25.030. Casing and Cementing". Alaska Legal Resource Center. March 2004 <http://touchngo.com/lglcntr/akstats/AAC/Title20/Chapter025/Section030.htm>.

"API Specifications 10". American Petroleum Institute Standards. Dec. 2004 <http://www.api.org>.

Banfill, P.F.G. "The Rheology of Fresh Cement and Concrete – A Review". Proceedings of the 11th International Cement Chemistry Congress. May 2003.

Benge, O.G., et al. "A New Low-Cost Permafrost Cementing System". SPE 10757 (March 1982).

"Cement". Wikipedia Online Encyclopedia. March 2004 <http://en.wikipedia.org/wiki/Cement>.

Cengel, Yunus A. Fundamentals of Thermal-Fluid Sciences. New York: McGraw Hill Publishing, 2001.

Davis, Neil. Permafrost: A Guide to Frozen Ground in Transition. Fairbanks: University of Alaska Press, 2001.

Dowling, Norman E. Mechanical Behavior of Materials, 2nd ed. Upper Saddle River: Prentice Hall, 1999.

Goodman, M.A. "Here's What to Consider When Cementing Permafrost". World Oil (1977): 81-87.

Heinhold, Thomas et al. "Analysis of Tensile Strength Test Methodologies For Evaluating Oil and Gas Wells". SPE 84565 (Oct 2003).

Hudson, J.A. et al. Engineering Rock Mechanics. New York: Pergamon Press, Inc., 1997.

Maier, L.F. et al. "Cementing Materials for a Cold Environment". Journal of Petroleum Technology (Oct 1971).

Morris, E.F. "Evaluation of Cement Systems for Permafrost". SPE 2824 (Feb. 1970).

Nelson, Erik B. and Philippe Drecq. "Special Cement Systems". Schlumberger Publications, 2001.

"Rheology". Schlumberger Oilfield Glossary. 2005 <http://www.glossary.oilfield.slb.com/>

Smith, Dwight K. Cementing, 2nd ed. SPE Monograph Volume 4, 1986.

Wagh, Arun. "Ceramicrete Fact Sheet". ANL Tech Transfer Advertisement. Chicago: Argonne National Laboratory, 2001.

Wagh, Arun, et. al. "Chemically Bonded Phosphate Ceramics: I, A Dissolution Model of Formation". J. Am. Ceramics Society 86[11]:1834-1844 (2003).

Wagh, Arun, et. al. "Laboratory Studies of Novel Phosphate-based Cements for Arctic Oil Field Applications". Oil and Gas Journal (2004).

Appendix A:

Alaskan statute 20 AAC 25.030 ~ Casing and Cementing

(a) A complete proposed well casing and cementing program must be submitted with an application for a Permit to Drill (Form 10-401). Unless modified or altered by pool rules established under 20 AAC 25.520, a well casing and cementing program must be designed to

(1) provide suitable and safe operating conditions for the total measured depth proposed;

(2) confine fluids to the wellbore;

(3) prevent migration of fluids from one stratum to another;

(4) ensure control of well pressures encountered;

(5) protect against thaw subsidence and freezeback effects within permafrost;

(6) prevent contamination of freshwater;

(7) protect significant hydrocarbon zones; and

(8) provide well control until the next casing is set, considering all factors relevant to well control including formation fracture gradients, formation pressures, casing setting depths, and proposed total depth.

(b) General well casing and cementing provisions are as follows:

(1) casing design and setting depth must be based on engineering and geologic factors relevant to the immediate vicinity, including the presence or absence of hydrocarbons, potential drilling hazards, and permafrost;

(2) for all casing strings on which blowout prevention equipment (BOPE) will be installed, cement may not be drilled out until sufficient compressive strength has been reached to obtain a valid formation integrity test;

(3) within permafrost intervals, fluids that have a freezing point above the minimum permafrost temperature may not be left in casing-by-casing annuli or inside the casing upon completion, suspension, or shutdown of well operations, without commission approval of an alternate method that the commission determines will prevent damage to the casing;

(4) if casing is subjected to prolonged drilling operations, the commission will, as necessary to verify casing integrity, require the casing to be pressure-tested, calipered, or otherwise evaluated by a method approved by the commission;

(5) if zonal coverage is required under (a) of this section, and the commission believes zonal isolation might not have been established, the commission will require a cement quality log or other method to demonstrate isolation of the zone.

(c) Specific well casing provisions are as follows:

(1) structural casing must be set by driving, jetting, or drilling to a minimum depth of 70 feet in offshore wells to support unconsolidated shallow strata, to provide hole stability for initial drilling operations, and to provide a competent anchor for a diverter system;

(2) for onshore wells, conductor casing must be set by driving, jetting, or drilling to a depth sufficient to provide anchorage for a diverter system, and for offshore wells, conductor casing must be set no less than 300 feet and no more than 1,000 feet below the mudline datum; however, the commission will

(A) approve a different casing setting depth if necessary to permit the casing shoe to be set in a competent formation or below formations that should be isolated; or

(B) authorize an operator to drill without setting conductor casing based upon information from wells drilled in the immediate vicinity and other available data, if the commission determines that the absence of conductor casing will not jeopardize well control;

(3) surface casing must be set below the base of all strata known or reasonably expected to serve as a source of drinking water for human consumption and at a depth sufficient to provide a competent anchor for BOPE;

(4) one or more intermediate casing strings must be set if required for protection of oil or gas or for protection against abnormally geo-pressured strata and lost circulation zones, or if otherwise required by well conditions;

(5) production casing must be set and cemented through, into, or just above the production interval;

(6) slotted liners, pre-perforated liners, and screens installed below a production packer are considered production equipment and not casing.

(d) Specific well casing cementing provisions are as follows:

(1) if structural casing is set by drilling or jetting, the structural casing must be cemented with sufficient cement to fill the annular space from the shoe to the surface;

(2) if conductor casing is set by drilling or jetting, the conductor casing must be cemented by filling the annular space with cement from the shoe to the surface; if BOPE is to be installed on the conductor casing, the adequacy of the cement to contain potential wellbore pressures and fluids must be demonstrated by a formation integrity test;

(3) conductor casing cement may be washed out to a depth not exceeding the depth of the structural casing shoe, if installed;

(4) surface casing must be cemented by filling the annular space with cement from the shoe to the surface; however, if cement does not circulate to the surface, if an excessive quantity of cement circulates to the surface, or if the formation integrity test shows an inadequate cement job,

(A) the operator shall notify the commission before drilling ahead; and

(B) the commission will require

(i) a cement quality log or other approved method to evaluate the adequacy of the cement to contain potential wellbore pressures and fluids; and

(ii) remedial action as necessary to meet the requirements of (a) of this section before drilling ahead;

(5) intermediate and production casing must be cemented with sufficient cement to fill the annular space from the casing shoe to a minimum of 500 feet above all significant hydrocarbon zones and abnormally geo-pressured strata or, if zonal coverage is not required under (a) of this section, from the casing shoe to a minimum of 500 feet above

the casing shoe; if indications of improper cementing exist, such as lost returns, or if the formation integrity test shows an inadequate cement job, remedial action must be taken; **(6)** if the intermediate or production string is a liner, a minimum of 100 feet overlap between the outer and inner strings is required; the interval of overlap must be made pressure competent and must be pressure-tested in accordance with (e) of this section; **(7)** for intermediate or production casing in a service well used for injection, a cement quality log or other evaluation log approved by the commission must be run to demonstrate isolation of the injected fluids to the approved interval.

(e) A casing pressure test must be performed if BOPE is to be installed on a casing. The casing must be tested to hold a surface pressure equal to 50 percent of the required working pressure of the BOPE as specified in the Permit to Drill under 20 AAC 25.035(e) (3) or 20 AAC 25.036(c) (3). The results of this test and any subsequent tests of the casing must be recorded as required by 20 AAC 25.070(1) .

(f) Except for through-tubing drilling, a formation integrity test must be performed if BOPE is installed on a casing. The test must be performed to a predetermined equivalent mud weight, leak-off, or fracture pressure as specified in the application for the Permit to Drill. The test must be conducted after drilling out of the casing shoe into at least 20 feet but not more than 50 feet of new formation. The test results must demonstrate that the integrity of the casing shoe is sufficient to contain anticipated wellbore pressures identified in the application for the Permit to Drill. The test procedure followed and the data from the test and any subsequent tests of the formation must be recorded as required by 20 AAC 25.070(1) .

(g) Upon request of the operator, the commission will, in its discretion, approve variances from the requirements of (b) - (f) of this section to allow for special or unusual conditions if the design requirements of (a) of this section are satisfied.

Authority:

AS 31.05.030

Appendix B:

Discarded Consistometer Data

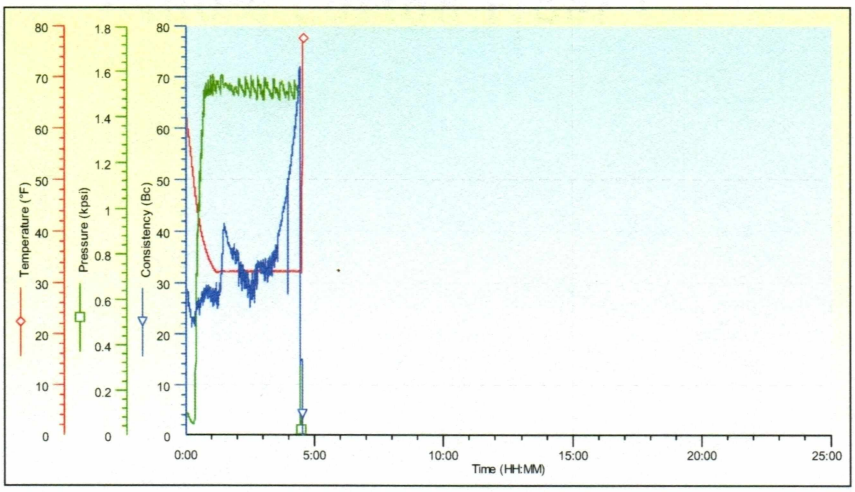


Figure 42: Discarded run #1

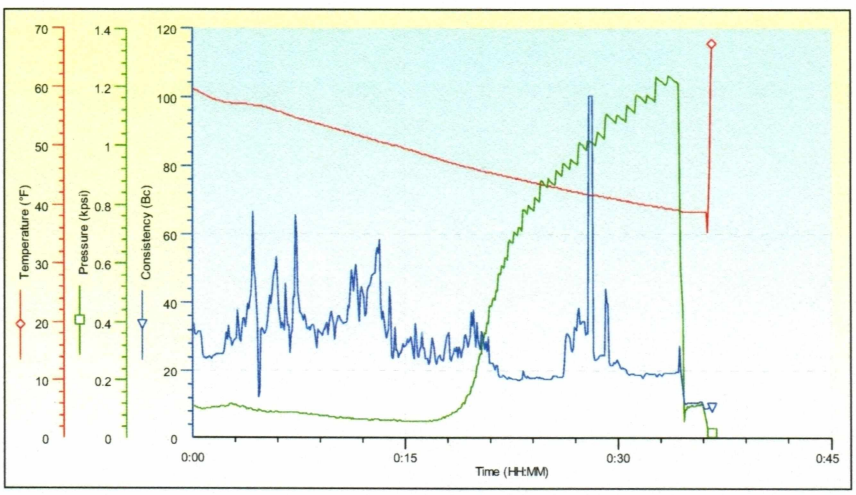


Figure 43: Discarded run #2

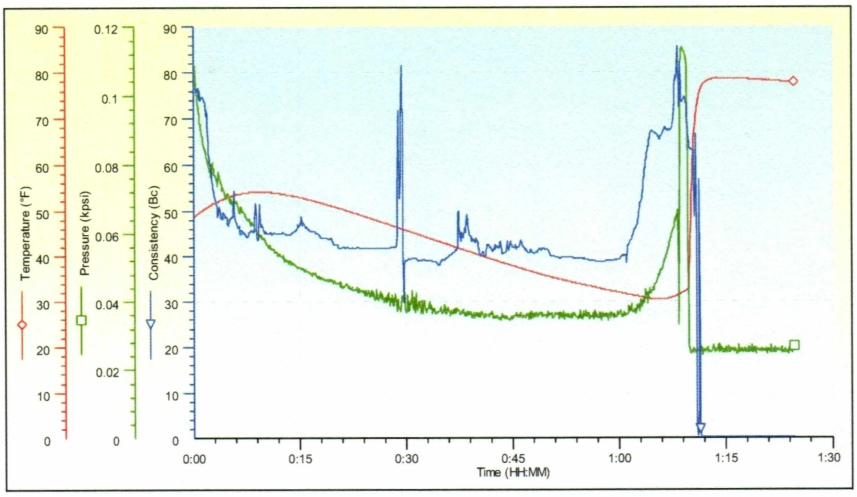


Figure 44: Discarded run #3

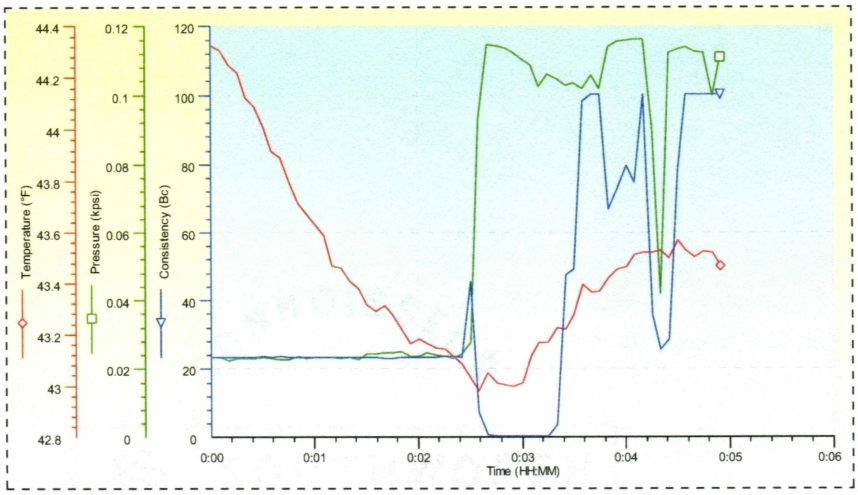


Figure 45: Discarded run #4